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GENERAL EXPONENTIAL-TYPE FUNCTIONS IN ATOMIC CALCULATIONS

ROBERT H. CARRIER

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GENERAL EXPONENTIAL-TYPE FUNCTIONS IN ATOMIC CALCULATIONS

by

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Robert H. Carrier

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ABSTRACT

GENERAL EXPONENTIAL-TYPE

FUNCTIONS IN ATOMIC CALCULATIONS

by

ROBERT H. CARRIER

General exponential type functions are employed with varying degrees of success in numerous and diverse atomic calculations. Various formulations of the independent particle model are treated. Energies are calculated and hyperfine splittings are computed for doublet lithium and triplet helium. Electron correlations in the formalisms of multiconfiguration interaction and inclusion of the inter-electronic separation as a coordinate in the wavefunction are considered. Formulas for pertinent transcendental function differentials are also derived.

SECTION I

INTRODUCTION

General exponential-type functions (GETF) were used with success in a simple hydrogen molecule calculation[1] and in a single-configuration closed shell representation of the 1^1S state of helium.[2] Therefore it is of interest that these functions be employed in the calculation of energies of other atomic systems. They should also be utilized in diverse types of atomic calculations.

The first part of this paper considers single configuration wavefunctions; i.e., representations of the independent particle model. The energies of each of the following systems were calculated according to either one or several various formalisms[3]; the hydride ion (1^1S), the helium atom (1^1S, 2^1S, 2^3S), the lithium atom (^2S), the beryllium atom (^1S), the boron atom (^2P), and the carbon atom (^1S, ^1D, ^3P). The spin and charge densities at the nucleus were determined for various three basis-function lithium wave functions and the hyperfine splitting constant was calculated for the lowest triplet state of helium.

The second portion of the dissertation deals with correlated wavefunctions of the ground state and the lowest triplet state of helium. Multiconfiguration interaction[4]

involving modifications of the Taylor-Parr wavefunction[5], and attempts to approach the S-limit[6] with both split and closed shell configurations are presented. Wavefunctions including the interelectronic separation explicitly are treated. Calculations involving a simple function of the Hylleraas coordinates "u" and "s"[7] were first undertaken. Later, closed and split shell functions in r_1 and r_2 combined with the correlation function $1+cr_{12}$[8] were considered.

A lithium wavefunction of the type analogous to that of E. Bright Wilson[9] and double-zeta functions[10] for the hydride ion and the helium atom were optimized using a gradient method[11] rather than a non-derivative pattern search method.[12] The energy expression for the double-zeta calculations is differentiated analytically with respect to the variational parameters.

Comparing various double precision calculations with corresponding single precision calculations on double-zeta helium wavefunctions, one discovers an error of three to five units in the seventh place; hence, all single precision energy values are reported to six places. It is noted that the energy is somewhat insensitive to a change in the fourth place and totally insensitive to a change in the fifth place of a variational parameter, therefore these parameters are reported to four places after the decimal point. The double

precision energies and parameters are reported to eight significant figures. All work except the multiconfiguration interactions, the three basis-function lithium calculations, and the excited states of helium has been done on an I.B.M. model 360/44; the latter were run on a model 360/50.

SECTION II

GENERAL EXPONENTIAL-TYPE FUNCTIONS AND THE INDEPENDENT-PARTICLE MODEL

1. INTRODUCTION

The independent-particle model is that interpretation of atomic structure which describes interelectronic interactions in an average fashion only. More specifically, each electron is assumed to move in the averaged central potential field of the others.[13] There are several procedures based on this model by which approximate wavefunctions governing a system may be obtained. These are the Hartree-Fock method (HF) (the oldest and most widely used[14]), the unrestricted Hartree-Fock method (UHF)[15], and the extended Hartree-Fock method (EHF).[3,16]

The HF approximation, also called by others the restricted Hartree-Fock method (RHF)[17], is that formalism by which the wavefunctions of a system are represented by single Slater determinants which are eigenfunctions of the spin operator $\mathcal{S}^2$ and the angular momentum operator $\mathcal{L}^2$ or, in certain open shell cases, by a set of orthogonal determinants which are projected from one determinant which does not satisfy the above conditions but which does contain the de-

sired energy state mixed in with others.[14] For example, the ^1S state of carbon may be projected from the determinant $|\, 1s\ 1\bar{s}\ 2s\ 2\bar{s}\ p_0\ \bar{p}_0\,|$ which contains a mixture of the ^1S and the ^1D states. The orbitals which form the determinants are subject to have two restrictions; that they be orthonormal and that equivalence of each n,l group be observed (the same radial function for each group).[18]

The UHF method is that procedure which allows the wavefunction of a system to be represented as a single determinant constructed from different orbitals for different spins with the orthonormality requirement imposed. These wavefunctions are generally not eigenfunctions of $\mathcal{S}^2$.

The EHF procedure describes the wavefunctions as a set of determinants which are eigenfunctions of $\mathcal{S}^2$ and $\mathcal{L}^2$ and which contain the same set of orbitals, a different one for each electron; for example, the core-polarized wavefunction for lithium, which will be discussed at length later.

2. THEORY AND METHOD

A. The Hamiltonian and the Determinantal Wavefunction

The Hamiltonian employed here is of the form;

$$\mathcal{H} = \sum_{i}^{N} h_i + \sum_{i<j}^{N} \frac{1}{r_{ij}} \qquad (1)$$

with the understanding that the nuclear mass is infinite and that relativistic effects are disregarded. Here

$$h_i = -\tfrac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \tag{2}$$

is known as the one-electron operator and $\frac{1}{r_{ij}}$, the inverse of the distance between electrons i and j, is the two-electron operator. The Laplacian operator can be expanded as

$$\nabla_i^2 = \frac{1}{r_i^2}(D_i - \mathcal{L}_i^2) \tag{3}$$

where

$$D_i = \frac{\partial}{\partial r_i} r_i^2 \frac{\partial}{\partial r_i} \tag{4}$$

is the radial operator, and

$$\mathcal{L}_i^2 = -\frac{1}{\sin\theta_i}\frac{\partial}{\partial\theta_i}\sin\theta_i\frac{\partial}{\partial\theta_i} - \frac{1}{\sin^2\theta_i}\frac{\partial^2}{\partial\varphi_i^2} \tag{5}$$

is the angular momentum for one electron. All terms are expressed in atomic units. The energy is calculated as

$$E = \frac{\langle\Psi|\mathcal{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \tag{6}$$

such that E is a minimum with respect to the variational parameters in Ψ , the wavefunction.

The minimization procedure for all but the calculations expected in the introduction (Section I) is a program called STEPIT furnished by Q. C. P. E.[20] and adapted for our usage under the name of MINMUM by J. J. Eberhardt.[1]

The single configuration wavefunctions are either single Slater determinants or linear combinations of Slater determinants whose coefficients are determined by projection. The determinant $|\chi_1(1)\chi_2(2)\cdots\chi_N(N)|$ may be expanded as $\mathcal{A}\prod_{k=1}^{N}\chi_k(k)$ where $\mathcal{A}$ is the antisymmetrizer defined as

$$\mathcal{A} = (N!)^{-\frac{1}{2}}\sum_{\mathcal{P}}(-1)^{p}\mathcal{P} \qquad (7)$$

[21]

where $\mathcal{P}$ is an operator which permutes the electrons in all possible ways up to N at a time, and p is the parity of the permutation. It can be noted that the expanded determinant contains N! terms. The orbitals $\chi_j(i)$ are composed of basis functions $\phi_k(i)$:

$$\chi_j(i) = \sum_{k=1}^{L} c_k \phi_k(i) \qquad (8)$$

where $$\phi_k(i) = \left(\rho(2\alpha_k)^{\frac{2n_k+1}{\rho}} / \Gamma\left(\frac{2n_k+1}{\rho}\right)\right)^{\frac{1}{2}} \cdot r_i^{n_k-1} e^{-\alpha_k r_i^{\rho}} Y_{\ell_k, m_k}(\theta_i, \phi_i) \cdot \sigma_k(i) \cdot \qquad (9)$$

Here $\sigma_k(i)$ is the spin function α or β (the parameter, α_k, is not to be confused with the spin function, α) and L is the length of the expansion.

B. Analytical Approximations to the Hartree-Fock Procedure

There have been devised some accurate analytical HF wavefunctions for two electron atoms[22] and for many electron atoms.[23] In order that these forms may suitably represent the behavior of the numerical HF wavefunctions, they must not only realize an accurate energy, but also must reproduce other atomic properties faithfully. This requires a many termed expansion.[24] The calculations presented in this paper are exploratory in nature and are not designed to represent the HF wavefunctions to any high degree of accuracy. These functions attempt only to reproduce the HF energies. However, expectation values of r^n (where n = -2, -1, 1, 2, 3, 4) are calculated for the double-zeta functions of the hydride ion and the helium atom, since these best reproduce the HF energies.

The determinantal wavefunctions of beryllium, boron and carbon in the energy states under study have two doubly occupied s-orbitals. One wishes to know whether the imposition of the orthogonality condition between these orbitals will restrict the variation, thus leading to a raising of the energy. It is stated that a single Slater determinant composed of doubly occupied orbitals is invariant to any kind of orthogonalization; also if a subset of the determinant be doubly occupied, the determinant containing the subset is invariant to any kind of orthogonalization procedure employed upon this subset.[25] The subset orthogonality invariance under Löwdin orthogonalization[26] may be demonstrated as follows:

let $$D = |s_1\overline{s_1}s_2\overline{s_2}(p)| \qquad (10)$$

(p) is the set of p-orbitals, if any. Now

$$S_k = \Delta^{-\frac{1}{2}}_{1k}\phi_1 + \Delta^{-\frac{1}{2}}_{2k}\phi_2. \quad (k=1,2) \qquad (11)$$

The superfluous electron designation has been omitted. For the case of the β spin function, a bar is placed above S_k, ϕ_1, ϕ_2. Substituting for S_k and being mindful of the properties of determinants:

$$D = (\Delta_{11}^{-\frac{1}{2}}\Delta_{22}^{-\frac{1}{2}} - \Delta_{12}^{-\frac{1}{2}}\Delta_{21}^{-\frac{1}{2}})\,|\,\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2(p)\,| \tag{12}$$

now $\Delta_{11}^{-\frac{1}{2}} = \Delta_{22}^{-\frac{1}{2}} = \frac{1}{2}\left[(1+\Delta)^{-\frac{1}{2}} + (1-\Delta)^{-\frac{1}{2}}\right]$

and $\Delta_{12}^{-\frac{1}{2}} = \Delta_{21}^{-\frac{1}{2}} = \frac{1}{2}\left[(1+\Delta)^{-\frac{1}{2}} - (1-\Delta)^{-\frac{1}{2}}\right]$ (13)

where $\Delta = \langle\phi_1|\phi_2\rangle$ is the overlap integral.[27]

Writing $|\,\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2(p)\,|$ as $\bar{D}$,

$$D = \frac{1}{1-\Delta^2}\,\bar{D} \tag{14}$$

thus $$E = \frac{\langle D|\mathcal{H}|D\rangle}{\langle D|D\rangle} = \frac{\langle\bar{D}|\mathcal{H}|\bar{D}\rangle}{\langle\bar{D}|\bar{D}\rangle} \tag{15}$$

Therefore, the energy of the four, five and six electron systems studied is not affected by this orthogonalization procedure.

In the above calculations, the contribution to the total energy which arises from the S_1 and S_2 doubly occupied orbitals will be designated as E_s:

$$E_S = \sum_{j,k}^{2}(\phi_j|\phi_k)\Delta_{jk}^{-1} + \sum_{k,l,p,q}^{2}(\phi_k\phi_l|\phi_p\phi_q)\left[2\Delta_{kl}^{-1}\Delta_{pq}^{-1} - \Delta_{kq}^{-1}\Delta_{lp}^{-1}\right]. \tag{16}$$

Here $\underset{\sim}{\Delta}^{-1}$ is the matrix of overlap integrals, $(\phi_j|\phi_K)$ and $(\phi_k\phi_l|\phi_p\phi_q)$ are the integrals $\int \phi_j^*(i) h_i \phi_k(i) d\tau_i$ and $\int \phi_k^*(i)\phi_l(i)\frac{1}{r_{ij}}\phi_p^*(j)\phi_q(j) d\tau_i d\tau_j$ respectively. For boron and carbon the total energy may be expressed as:

$$E = E_s + E_{sp} + E_p \tag{17}$$

The contribution between the s and p-orbitals to the energy is:

$$E_{sp} = n \sum_{i,j}^{2} [2(\phi_i\phi_j|pp) - (\phi_i p|p\phi_j)]\Delta^{-1}_{ij} . \tag{18}$$

The azimuthal quantum numbers of the p-orbitals are immaterial since the Clebsch-Gordon coefficients arising from the angular integrations between an s and any p_m (m=1, 0,-1) orbitals are the same.[29] The n is the number of p-orbitals in the determinant. For boron, triplet state carbon and singlet state carbon the p-orbital energy contributions are the following:

$$E_p = (p/p);\ \text{boron } (^2P)$$

$$E_p = 2(p|p) + (p_1p_1|p_{-1}p_{-1}) - (p_1p_{-1}|p_{-1}p_1);\ \text{carbon } (^3P) \tag{19}$$

$$E_p = 2(p|p) + (p_m p_m|p_m p_m);$$

m = 1 or 0 for the ^1D and the mixed ^1D, ^1S carbon states, respectively.

More must be said in conjunction with the ^1S carbon state, which state must be projected from the determinant, $|s_1\bar{s}_1 s_2\bar{s}_2 p_0\bar{p}_0|$. The angular momentum operator, O_k, takes on the following form:

$$O_k = \prod_{l \neq k} \left\{ 1 - \frac{\mathcal{L}^2 - k(k+1)}{(l-k)(l+k+1)} \right\}, \qquad (20)$$

where k is the total angular momentum quantum number of the desired state. In the above determinant $l = 0$ or 2; therefore

$$O_0 = 1 - \frac{1}{6}\mathcal{L}^2 \qquad (21)$$

The operator $\mathcal{L}^2$ may be decomposed as;

$$\mathcal{L}^2 = \mathcal{L}_+ \mathcal{L}_- + \mathcal{L}_z^2 - \mathcal{L}_z \qquad (22)$$

The step-up and step-down operators are defined as follows, and enjoy the subsequent properties;

$$\mathcal{L}_\pm = \sum_i \mathcal{L}_\pm(i) \qquad (23)$$

$$\mathcal{L}_\pm(i)\, Y_{l,m}(\theta_i, \phi_i) = [l(l+1) - m(m\pm1)]^{\frac{1}{2}} Y_{l,m\pm1}(\theta_i, \phi_i)$$

The z component angular momentum operator may be defined as, and has the following property:

$$\mathcal{L}_z = \sum_i \mathcal{L}_z(i)$$
$$\mathcal{L}_z(i)\, Y_{l,m}(\theta_i,\phi_i) = m Y_{l,m}(\theta_i,\phi_i) \tag{24}$$

Let $$D = \mathcal{A} \prod_k \chi_k(k) \tag{25}$$

where $$\chi_k(k) = R_k(k) Y_{l_k,m_k}(k)\, \sigma_k(k) . \tag{26}$$

Since $\mathcal{L}^2$ is symmetric relative to the electron coordinates it commutes with $\mathcal{A}$, then:

$$\mathcal{L}_\pm D = \mathcal{A} \sum_i a_i^\pm R_i(i) Y_{l_i,m_i\pm1}(i) \cdot \sigma_i(i) \prod_{k\neq i} \chi_k(k)$$

here $$a_i^\pm = [\, l_i(l_i+1) - m_i(m_i\pm1)\,]^{\frac{1}{2}} ; \tag{27}$$

as for the operator $\mathcal{L}_z$,

$$\mathcal{L}_z D = M D$$

where $$M = \sum_i m_i \tag{28}$$

Reassembling the angular momentum operator;

$$\mathcal{L}^2 D = \Big(\sum_i a_i^+ a_i^- + M(M-1)\Big) D + \sum_{i\neq j} a_i^+ a_j^- \mathcal{A}\, R_i(i) Y_{l_i,m_i+1}(i)\, \sigma_i(i) \cdot R_j(j) Y_{l_j,m_j-1}(j)\, \sigma_j(j) \prod_{k\neq i,j} \chi_k(k) \tag{29}$$

Let $$D_{m_1,m_2} = |s_1 \bar{s}_1 s_2 \bar{s}_2 p_{m_1} \bar{p}_{m_2}| \tag{30}$$

The application of the $\mathcal{L}^2$ operator on the mixed state determinant can be expressed as;

$$\mathcal{L}^2 D_{0,0} = 4D_{0,0} + 2D_{1,-1} + 2D_{-1,1} \ . \tag{31}$$

On applying the projection operator and normalizing;

$$\psi(^1S) = \frac{1}{\sqrt{3}}(D_{0,0} - D_{1,-1} - D_{-1,1}) \tag{32}$$

It is customary to minimize the wavefunction, $\psi\ (^1S)$.[31,32] However, the ^1S energy has been found here by projecting from $D_{0,0}$ after this determinant had been minimized.

The wavefunction used for lithium to approximate the HF energy (the three basis-function calculation is discussed in the next part of this subsection) is of the form:

$$\psi = |\chi_1 \bar{\chi}_1 \chi_2| \tag{33}$$

where the orbitals are defined as:

$$\chi_1 = \phi_1$$
$$\chi_2 = N_2(\delta\phi_1 + \lambda\phi_2). \tag{34}$$

Here the quantities N_2, λ and δ are:

$$N_2 = (\delta + 2\delta\lambda\langle\phi_1|\phi_2\rangle + \lambda^2)^{-\frac{1}{2}}$$
$$\lambda = -1/\langle\phi_1|\phi_2\rangle$$
$$\delta = 1 \qquad \text{(orthogonal } \chi_1, \chi_2\text{)} \qquad (35)$$
$$\delta = 0 \qquad \text{(nonorthogonal case).}$$

The energy expression may be written as:

$$E = \{[2 - \Delta^2 + N_2^2\delta - 2\Delta N_2\delta](\phi_1|\phi_1) + 2\lambda N_2(\delta N_2 - \Delta)(\phi_1|\phi_2) + N_2^2\lambda^2(\phi_2|\phi_2) + (1 + \delta N_2(N_2 - 2\Delta))(\phi_1\phi_1|\phi_1\phi_1) + 2N_2\lambda \cdot (\delta N_2 - \Delta)(\phi_1\phi_1|\phi_1\phi_2) + N_2^2\lambda^2 \cdot (2(\phi_1\phi_1|\phi_2\phi_2) - (\phi_1\phi_2|\phi_2\phi_1))\}/(1 - \Delta^2)$$

$$\Delta = 0 \qquad \text{(orthogonal } \chi_1, \chi_2\text{)} \qquad (36)$$
$$\Delta = \langle\phi_1|\phi_2\rangle \qquad \text{(nonorthogonal case).}$$

The wavefunction for the 2^3S state of helium is represented here as:

$$\psi = |\chi_1\chi_2|$$

where $$\chi_1 = \phi_1 \qquad (37)$$

and $$\chi_2 = N(\delta\phi_2 + \lambda\phi_3)$$

in which $$N = (\delta + 2\lambda\delta\langle\phi_2|\phi_3\rangle + \lambda^2)^{-\frac{1}{2}}$$

and $$\lambda = -\frac{\langle\phi_1|\phi_2\rangle}{\langle\phi_2|\phi_3\rangle}.$$

The parameter δ has the same meaning as before. The energy expression is

$$E = \{(\phi_1|\phi_1)+(1+\delta N^2)(\phi_2|\phi_2)+N^2\lambda^2(\phi_3|\phi_3)- 2\Delta N(\delta(\phi_1|\phi_2)+\lambda(\phi_1|\phi_3))+2N^2\delta\lambda\cdot(\phi_2|\phi_3)+N^2[\delta((\phi_1\phi_1|\phi_2\phi_2)-(\phi_1\phi_2|\phi_2\phi_1))+2\lambda\delta((\phi_1\phi_1|\phi_2\phi_3)-(\phi_1\phi_2|\phi_1\phi_3))+\lambda^2((\phi_1\phi_1|\phi_3\phi_3)-(\phi_1\phi_3|\phi_3\phi_1))]\}/(1-\Delta^2)$$

here $\Delta = 0$ (orthogonal χ_1, χ_2) (38)

$\Delta = \langle\phi_1|\phi_3\rangle$ (nonorthogonal case)

The simpler nonorthogonal wavefunction for these two systems are calculated for the sake of discussion even though they do not strictly fall under the analytical HF scheme.

For the simplest systems considered, the 1^1S state of helium and H^-;

$$\psi = |\chi\bar{\chi}|$$

and $$E = 2(\chi|\chi)+(\chi\chi|\chi\chi) \quad (39)$$

The energy expression and its derivatives with respect to the variation parameters for the double-zeta wavefunction can be found in appendix III. The integrals over the basis functions are to be found in appendix II, unless stated otherwise. The details of the integrations can be found elsewhere.[1]

C. More Advanced Hartree-Fock Approximations and Hyperfine Splitting

The UHF and EHF approximations allow the electron of a system additional freedom since now the orbitals of the same, n,l group but of different spin states, m_s, are not constrained to the same radial dependence. According to the variational principle, the lifting of this restriction should produce a lower energy. These methods make one more conscious of the role played by spin in the wavefunction. The basic differences among the HF, UHF and EHF methods acutely affect the behavior of the wavefunction at the nucleus. The spin density, which governs the phenomenon of hyperfine splitting in atoms is particularly most sensitive to this behavior.[18] It is proper that a short exposition on the action of the spin angular momentum operator upon a Slater determinant be given.

The decomposition of $\mathcal{S}^2$ is analogous to that of $\mathcal{L}^2$; namely, where

$$\mathcal{S}^2 = \mathcal{S}_+\mathcal{S}_- + \mathcal{S}_z(\mathcal{S}_z - 1) \qquad (40)$$

$$\mathcal{S}_\pm = \sum_i \mathcal{S}_\pm(i)$$

and $$\mathcal{S}_z = \sum_i \mathcal{S}_z(i).$$

In order to establish the action of the one-electron operators, $\mathcal{S}_\pm(i)$ and $\mathcal{S}_z(i)$ on the spin functions

$\sigma(i)$, the matrix representations of these operators and the vector form of $\sigma(i)$ must be employed:

$$\underset{\sim}{S}_+(i) = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} \qquad \underset{\sim}{S}_-(i) = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}$$

$$\underset{\sim}{S}_z(i) = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$$\underset{\sim}{\alpha}(i) = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \qquad \underset{\sim}{\beta}(i) = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{41}$$

By the multiplication of vectors by matrices,

$$\begin{aligned} \underset{\sim}{S}_+(i)\,\underset{\sim}{\alpha}(i) &= 0 & \underset{\sim}{S}_+(i)\,\underset{\sim}{\beta}(i) &= \underset{\sim}{\alpha}(i) \\ \underset{\sim}{S}_-(i)\,\underset{\sim}{\alpha}(i) &= \underset{\sim}{\beta}(i) & \underset{\sim}{S}_-(i)\,\underset{\sim}{\beta}(i) &= 0 \\ \underset{\sim}{S}_z(i)\,\underset{\sim}{\alpha}(i) &= \tfrac{1}{2}\underset{\sim}{\alpha}(i) & \underset{\sim}{S}_z(i)\,\underset{\sim}{\beta}(i) &= -\tfrac{1}{2}\underset{\sim}{\beta}(i) \end{aligned} \tag{42}$$

one can deduce immediately that,

$$\begin{aligned} \underset{\sim}{S}_z D &= \frac{n_\alpha - n_\beta}{2} D = M_S D \\ \underset{\sim}{S}_+(i)\,\underset{\sim}{S}_-(i)\,\underset{\sim}{\sigma}(i) &= \underset{\sim}{\sigma}(i) \\ \underset{\sim}{S}_+(i)\,\underset{\sim}{S}_-(j)\,\underset{\sim}{\beta}(i)\underset{\sim}{\alpha}(j) &= \underset{\sim}{\alpha}(i)\,\underset{\sim}{\beta}(j) \end{aligned} \tag{43}$$

The other combinations lead to a result of zero. Hence;

$$S^2 D = \left\{ \sum_\sigma \mathcal{P}_{\alpha\beta} + \frac{1}{4}\left[(n_\alpha - n_\beta)^2 + 2(n_\beta + n_\alpha) \right] \right\} D \tag{44}$$

where $\sum_\sigma \mathcal{P}_{\alpha\beta}$ is an operator which exchanges the α and β spin functions of the determinant in every possible manner, n_β and n_α is the number of β and α spins in the determinant.[33]

The wavefunctions employed for the UHF approximation on lithium are not eigen-functions of $\mathcal{S}^2$ [34,35] but the expectation value of this operator, $\langle \mathcal{S}^2 \rangle$, may be found, thus determining how much quadruplet state is mixed with the desired doublet state. If the UHF wavefunction for lithium is represented by D_2 where,

$$\begin{aligned} D_1 &= |\bar{\chi}_1 \chi_2 \chi_3| \\ D_2 &= |\chi_1 \bar{\chi}_2 \chi_3| \\ D_3 &= |\chi_1 \chi_2 \bar{\chi}_3| \end{aligned} \tag{45}$$

then $$\langle \mathcal{S}^2 \rangle = \frac{\langle D_2 | \mathcal{S}^2 | D_2 \rangle}{\langle D_2 | D_2 \rangle}$$

$$= \frac{7}{4} + (\langle D_1 | D_2 \rangle + \langle D_2 | D_3 \rangle) / \langle D_2 | D_2 \rangle.$$

However, in the UHF approximation χ_1 and χ_3 are orthogonal, thus;

$$\langle \mathcal{S}^2 \rangle = \frac{7}{4} - \langle \chi_1 | \chi_2 \rangle - \langle \chi_2 | \chi_3 \rangle \tag{46}$$

The EHF method demands that the wavefunction be an eigenfunction of $\mathcal{S}^2$. This requirement can be met by applying the appropriate spin projection operator which may be written in the form;

$$^{2S+1}O = \prod_{k \neq S} \frac{\mathcal{S}^2 - k(k+1)}{S(S+1) - k(k+1)} \tag{47}$$

where s is the spin angular momentum of the desired state.[36] Since k = 1/2 and 3/2, and s = 1/2 for the case of the doublet component of D_2, the projection operator reduces to,

$$^2O = \frac{5}{4} - \frac{1}{3}S^2 \tag{48}$$

Application of this operator to D_2 obtains the following;

$$\Psi(^2S) = \frac{1}{3}(2D_2 - D_1 - D_3) \tag{49}$$

It might be indicated that this wavefunction does not lead to a much better energy than the HF wavefunction.[37] A slightly more improved energy is obtained by projecting out the proper wavefunction from D_2 with a group operator (the GF method).[38,39] However, the details of this procedure are much too complex to discuss here. There is another manner of expressing Ψ (^2S) in which the two core orbitals are polarized; that is, χ_1 and χ_2 enjoy an equal share of both α and β spins and the outer orbital, χ_3, is relegated to one particular spin, in this case to the α spin.

$$\Psi(^2S) = D_2 - D_1 \tag{50}$$

which is an eigenfunction of S^2. EHF energies and other properties have been calculated by a numerical method[40,41], and by the GI method[42] which employs Wigner projection operators based on orthogonal representations for the symmetric

group.[43] The energies obtained by these methods are considerably improved over the HF approximation.

Hyperfine structure refers to an exceedingly small splitting (1-10,000 Mc/sec) of atomic spectral lines attributed to the interaction of electronic moments with nuclear electric and magnetic moments. From the parity of the operators which arise from the multipole expansions of the nuclear magnetic and electric moments, only 2^{2n}-pole electric components and 2^{2n-1}-pole magnetic components contribute to hyperfine splitting[44] (here n is a positive integer). In the treated cases of ^3S helium and ^2S lithium the dipolar and orbital interactions vanish leaving only the Fermi contact term to govern the hyperfine splitting.[18] Since this interaction takes place at the nucleus, only functions of s-symmetry can contribute to hyperfine structure because only they can describe a non-zero density at the nucleus. More precisely, hyperfine splitting depends upon the spin density at the nucleus, since s-orbitals possess only spin angular momenta.

The Hamiltonian for hyperfine interaction is defined by the Fermi contact term in this approximation

$$H_{CO} = \frac{8\pi}{3}\left(\frac{\beta_n}{I}\right)\left(\frac{\beta_e}{S}\right) I \cdot \sum_i S_z(i)\,\delta(r_i) \qquad (51)$$

where β_n, β_e are the nuclear and electronic magnetic moment constants in Bohr magnetons, I and S are the nuclear and electronic spins, and $\delta(r_i)$ is a delta function defining the charge density of electron i at the nucleus.[45] This Hamiltonian may be rendered in the form;

$$\langle H_{co} \rangle = c_s Q(0) \tag{52}$$

where c_s is a constant depending upon the system and Q(0) is the spin density at the nucleus computed as;

$$Q(0) = \frac{1}{S} \langle \Psi | \sum_i \delta_z(i) \delta(r_i) | \Psi \rangle / \langle \Psi | \Psi \rangle . \tag{53}$$

It may be noted that the charge density at the nucleus, D(0); is computed as;

$$D(0) = \langle \Psi | \sum_i \delta(r_i) | \Psi \rangle / \langle \Psi | \Psi \rangle . \tag{54}$$

For a single basis function and a single electron,

$$\langle \delta(r_i) \rangle = \phi_i^2(0)$$

and

$$\langle \delta_z(i) \delta(r_i) \rangle = \pm \tfrac{1}{2} \phi_i^2(0) \tag{55}$$

depending on the spin function attached to this particular space function.

A few calculations were carried out on lithium employing wavefunctions containing three basic functions. For the HF, UHF and EHF methods the applicable wavefunctions are;

$$\Psi_{HF} = |\chi_1 \bar{\chi}_1 \chi_3|$$
$$\Psi_{UHF} = |\chi_1 \bar{\chi}_2 \chi_3|$$
$$\Psi_{EHF} = |\chi_1 \bar{\chi}_2 \chi_3| - |\bar{\chi}_1 \chi_2 \chi_3| \qquad (56)$$

where $\chi_1 = \phi_1$, $\chi_2 = \phi_2$

$\chi_3 = N(\delta\phi_2 + \lambda\phi_3)$ case 1

$\chi_3 = N(\delta\phi_1 + \lambda\phi_3)$ case 2

The first definition of χ_3 is used for the HF and EHF schemes, both definitions of χ_3 are employed in the UHF method since the wavefunction is unsymmetrical with respect to χ_1 and χ_2. In the following expressions the values of the constants N, δ and λ are defined as;

$$N = (\delta + 2\lambda\delta\langle\phi_n|\phi_3\rangle + \lambda^2)^{-\frac{1}{2}} \qquad n = 1 \text{ or } 2$$
$$\delta = 0 \text{ or } 1 \qquad (57)$$

where $\lambda = -\dfrac{\langle\phi_1|\phi_n\rangle}{\langle\phi_1|\phi_3\rangle}$ $\qquad n = 1 \text{ or } 2$

for orthogonal cases; otherwise λ is treated as a variational parameter.

The expectation value expressions, Q(0), D(0) and $\langle S^2 \rangle$ are to be given for the various approximations. It should be noted that for finite, non-zero and physically meaningful values of Q(0) and D(0), the quantum numbers n_1 and n_2 are constrained to unity when these quantities are to be calculated.

$$
\begin{aligned}
E_{HF} = {} & 2(\phi_1|\phi_1) + (\phi_1\phi_1|\phi_1\phi_1) + N^2 \cdot \\
& \{(\phi_2|\phi_2) + 2\lambda(\phi_2|\phi_3) + \lambda^2(\phi_3|\phi_3) + \\
& 2(\phi_1\phi_1|\phi_2\phi_2) + 4\lambda(\phi_1\phi_1|\phi_2\phi_3) + \\
& 2\lambda^2(\phi_1\phi_1|\phi_3\phi_3) - (\phi_1\phi_2|\phi_2\phi_1) - \\
& 2\lambda(\phi_1\phi_2|\phi_1\phi_3) - \lambda^2(\phi_1\phi_3|\phi_3\phi_1)\}
\end{aligned}
\tag{58}
$$

$$Q(0) = N^2 \phi_2^2(0)$$

$$D(0) = 2\phi_1^2(0) + N^2\phi_2^2(0)$$

$$\langle S^2 \rangle = 3/4$$

in this approximation $\langle \chi_1 | \chi_3 \rangle = 0$ and $\delta = 1$.

$$
\begin{aligned}
E_{UHF_1} = {} & (\phi_1|\phi_1) + (\phi_2|\phi_2) + (\phi_1\phi_1|\phi_2\phi_2) + \\
& N^2\{(\phi_2|\phi_2) + 2\lambda(\phi_2|\phi_3) + \lambda^2(\phi_3|\phi_3) + \\
& (\phi_1\phi_1|\phi_2\phi_2) + 2\lambda(\phi_1\phi_1|\phi_2\phi_3) + \\
& \lambda^2(\phi_1\phi_1|\phi_3\phi_3) - (\phi_1\phi_2|\phi_2\phi_1) - 2\lambda \cdot \\
& (\phi_1\phi_2|\phi_3\phi_1) - \lambda^2(\phi_1\phi_3|\phi_3\phi_1) + \\
& (\phi_2\phi_2|\phi_2\phi_2) + 2\lambda(\phi_2\phi_3|\phi_2\phi_3) \\
& + \lambda^2(\phi_2\phi_3|\phi_3\phi_3)\}
\end{aligned}
\tag{59}
$$

$$Q(0) = \phi_1^2(0) + \phi_2^2(0)(N^2-1)$$

$$D(0) = \phi_1^2(0) + \phi_2^2(0)(N^2+1)$$

$$\langle S^2 \rangle = \frac{7}{4} - \langle \phi_1 | \phi_2 \rangle^2 - N^2(1+\lambda\langle \phi_2 | \phi_3 \rangle)^2.$$

For the second case:

$$\begin{aligned} E_{UHF_2} = {} & (\phi_1|\phi_1)+(\phi_2|\phi_2)+(\phi_1\phi_1|\phi_2\phi_2) + \\ & N^2\{(\phi_1|\phi_1)+2\lambda(\phi_1|\phi_3)+\lambda^2(\phi_3|\phi_3)+ \\ & \lambda^2(\phi_1\phi_1|\phi_3\phi_3)-\lambda^2(\phi_1\phi_3|\phi_3\phi_1)+ \\ & (\phi_1\phi_1|\phi_2\phi_2)+2\lambda(\phi_1\phi_3|\phi_2\phi_2)+ \\ & \lambda^2(\phi_2\phi_2|\phi_3\phi_3)\} \end{aligned} \tag{60}$$

$$Q(0) = \phi_1^2(0)(N^2+1) - \phi_2^2(0)$$

$$D(0) = \phi_1^2(0)(N^2+1) + \phi_2^2(0)$$

$$\langle S^2 \rangle = \frac{7}{4} - \langle \phi_1|\phi_2\rangle^2 - N^2(\langle \phi_1|\phi_2\rangle + \lambda\langle \phi_2|\phi_3\rangle)^2.$$

For both case $\langle \chi_1 | \chi_3 \rangle = 0$ and $\delta = 1$. Finally,

$$\begin{aligned} E_{EHF} = {} & \{(\phi_1|\phi_1)C_{11} + (\phi_1|\phi_2)C_{12} + (\phi_2|\phi_2)C_{22} + \\ & (\phi_1|\phi_3)C_{13} + (\phi_2|\phi_3)C_{23} + (\phi_3|\phi_3)C_{33} + \\ & 2(1+\delta N^2(1-S_2))(\phi_1\phi_1|\phi_2\phi_2) + \\ & (2-\delta N^2(1+2S_2))(\phi_1\phi_2|\phi_2\phi_1) + N^2[\\ & \lambda^2(2(\phi_1\phi_1|\phi_3\phi_3)-(\phi_1\phi_3|\phi_3\phi_1)+2(\phi_2\phi_2|\phi_3\phi_3) \\ & -(\phi_2\phi_3|\phi_3\phi_2))+2\lambda(2\delta-S_2)(\phi_1\phi_1|\phi_2\phi_3) - \\ & 2\lambda(\delta+S_2)(\phi_1\phi_2|\phi_3\phi_1)+2\lambda(3\delta S_0-S_1)\cdot \\ & (\phi_1\phi_3|\phi_2\phi_2)-2\lambda(\delta S_0+S_1)(\phi_1\phi_2|\phi_2\phi_3)+ \\ & 2\delta\lambda^2(2(\phi_1\phi_2|\phi_3\phi_3)-(\phi_1\phi_3|\phi_3\phi_2))+2\delta\cdot \\ & (S_0-2S_1)(\phi_1\phi_1|\phi_1\phi_2)+2\lambda S_0\cdot \\ & (\phi_2\phi_2|\phi_2\phi_3)+\delta(\phi_2\phi_2|\phi_2\phi_2)]\}/\Delta \end{aligned} \tag{61}$$

$$D(0) = (c_{11}\phi_1^2(0) + c_{12}\phi_1(0)\phi_2(0) + c_{22}\phi_2^2(0))/\Delta$$

$$Q(0) = (N^2S_2^2\phi_1^2(0) + (c_{12} - 4(S_0 - N^2S_1S_2))\phi_1(0)\phi_2(0) + (c_{22} - 2(1 - N^2S_1^2))\phi_2^2(0))/\Delta$$

$$\langle S^2 \rangle = 3/4$$

here

$$\Delta = 2 + 2S_0^2 - N^2(S_1^2 + S_2^2 + 2S_0S_1S_2)$$

$$c_{11} = 2 - N^2S_2^2$$

$$c_{12} = 2(2S_0 - N^2S_1S_2 - \delta N(S_1 + S_0S_2))$$

$$c_{22} = 2 - N^2S_1^2 - 2N\delta(S_2 + S_0S_1) + 2\delta N^2(1 + S_0)^2$$

$$c_{13} = -2\lambda N^2(S_1 + S_0S_2)$$

$$c_{23} = -2\lambda N^2(S_2 + S_0S_1)(2\delta + 1)$$

$$c_{33} = 2\lambda^2N^2(1 + S_0^2)$$

and

$$S_0 = \langle \phi_1 | \phi_2 \rangle$$

$$S_1 = \delta\langle \phi_1 | \phi_2 \rangle + \lambda\langle \phi_1 | \phi_3 \rangle$$

$$S_2 = \delta + \lambda\langle \phi_2 | \phi_3 \rangle.$$

For the EHF approximation, runs were made on both $\langle \chi_1 | \chi_3 \rangle = 0$ and $\langle \chi_1 | \chi_3 \rangle \neq 0$, and also for $\delta = 0$. The constant c_s employed to calculate the hyperfine splittings was 3474.38 Mc/sec.[35]

Some other helium wavefunctions were studied; namely, the EHF wavefunction for the 1^1S state and the wavefunction for the 2^1S excited state. These wavefunctions may be

expressed as;

$$\Psi = |\chi_1 \bar{\chi}_2| + |\chi_2 \bar{\chi}_1| \qquad (62)$$

where $\chi_1 = \phi_{11} + \lambda_1 \phi_{12}$

and $\chi_2 = \phi_{21} + \lambda_2 \phi_{22}$

The energy expression may be written as;

$$\begin{aligned} E = 2[& (\phi_{11}|\phi_{11}) + (\phi_{21}|\phi_{21}) + 2(\phi_{11}|\phi_{21}) + \\ & 2\lambda_1(\phi_{11}|\phi_{12}) + 2\lambda_1(\phi_{12}|\phi_{21}) + 2\lambda_2(\phi_{21}|\phi_{22}) \\ & + 2\lambda_2(\phi_{11}|\phi_{22}) + \lambda_1^2(\phi_{12}|\phi_{12}) + \lambda_2^2(\phi_{22}|\phi_{22}) \\ & + 2\lambda_1\lambda_2(\phi_{12}|\phi_{22}) + (\phi_{11}\phi_{11}|\phi_{21}\phi_{21}) + \\ & (\phi_{11}\phi_{21}|\phi_{21}\phi_{11}) + 2\lambda_2((\phi_{11}\phi_{11}|\phi_{21}\phi_{22}) + \\ & (\phi_{11}\phi_{22}|\phi_{21}\phi_{11})) + \lambda_2^2((\phi_{11}\phi_{11}|\phi_{22}\phi_{22}) + \\ & (\phi_{11}\phi_{22}|\phi_{22}\phi_{11})) + 2\lambda_1((\phi_{11}\phi_{12}|\phi_{21}\phi_{21}) + \\ & (\phi_{11}\phi_{21}|\phi_{21}\phi_{12})) + 4\lambda_1\lambda_2((\phi_{11}\phi_{12}|\phi_{21}\phi_{22}) + \\ & (\phi_{11}\phi_{22}|\phi_{21}\phi_{12})) + 2\lambda_1\lambda_2^2((\phi_{11}\phi_{12}|\phi_{22}\phi_{22}) + \\ & (\phi_{11}\phi_{22}|\phi_{22}\phi_{12})) + \lambda_1^2((\phi_{12}\phi_{12}|\phi_{21}\phi_{21}) + \\ & (\phi_{12}\phi_{21}|\phi_{21}\phi_{12})) + 2\lambda_1^2\lambda_2((\phi_{12}\phi_{12}|\phi_{21}\phi_{22}) + \\ & (\phi_{12}\phi_{22}|\phi_{21}\phi_{12})) + \lambda_1^2\lambda_2^2((\phi_{12}\phi_{12}|\phi_{22}\phi_{22}) + \\ & (\phi_{12}\phi_{22}|\phi_{22}\phi_{12}))] / [2 + \lambda_1^2 + \lambda_2^2 + \\ & 2\langle\phi_{11}|\phi_{21}\rangle + 2\lambda_1\langle\phi_{11}|\phi_{12}\rangle + 2\lambda_2\langle\phi_{21}|\phi_{22}\rangle + \\ & 2\lambda_1\langle\phi_{12}|\phi_{21}\rangle + 2\lambda_2\langle\phi_{11}|\phi_{22}\rangle + 2\lambda_1\lambda_2\langle\phi_{12}|\phi_{22}\rangle]. \end{aligned}$$

(63)

For the 2^1S state of helium three experiments were conducted. For excited state wavefunctions the conditions of the variational principle are violated if these are not orthogonal to the ground state, thus unacceptably low energies may result.[46] The first experiment, then, entailed the construction of a 2^1S wavefunction consisting of orthogonal orbitals but which was itself not orthogonal to the ground state. The variation may be so constrained as to produce very high energies.[47] The first wavefunction was therefore made orthogonal to the ground state as expressed by the double-zeta HF helium function, calculated in this paper, to determine if this did indeed occur for the cases under study. Lastly, the orbitals were constructed not orthogonal but the total wavefunction was made orthogonal to the previously mentioned HF function. The energy arising from this excited state wavefunction is designated by some authors as a Hartree-Fock energy[48], but the form of the wavefunction is specifically that of an EHF wavefunction since the two determinants which compose the configuration are not orthogonal. It must be noted for the orbitals considered (either a single basis function or a linear combination of two basis functions) that the 2^1S EHF function cannot be made orthogonal to the 1^1S EHF wavefunction.

Finally, the hyperfine splitting of the triplet state of helium was determined (the singlet states of helium by virtue of their vanishing total spin angular momentum exhibit no splitting). Hence,

$$Q(0) = \frac{1}{2}\left(\phi_1^2(0) + N^2 \phi_2^2(0) \right) \tag{64}$$

(refer to equation 38, orthogonal case) and

$$c_s = 8\pi \times 202.990 \text{ Mc/sec.}^{49} \tag{65}$$

3. RESULTS

The following five tables display the results of the calculations proposed in the prior subsection. Table I contains the parameters for the various HF calculations exclusive of the 2^3S helium atom, the three basis-function lithium calculation, and the double-zeta helium and hydride calculations. The parameters and energy values as well as some hyperfine splittings and charge densities at the nucleus for the three basis-function lithium wavefunctions are presented in Table II. Data on the excited states of helium as well as the ground state EHF wavefunction are to be found in Table III. The functions here are taken to be of the form;

$$\psi^{1,3} = |\chi\bar{\chi}'| \pm |\chi'\bar{\chi}| \tag{66}$$

with the plus sign for the singlet state and the minus sign for the triplet state wavefunction. The basis functions in equation 63 are rendered from ϕ_{11}, ϕ_{12}, ϕ_{21}, ϕ_{22} to ϕ_1, ϕ_2, ϕ_1', ϕ_2', respectively; and the basis functions in equation 38; namely, ϕ_1, ϕ_2 and ϕ_3 are redesignated as ϕ_1, ϕ_1', and ϕ_2'. Table IV contains information about the double precision calculations on the 1^1S state of the hydride ion and the helium atom and the ^2S state of lithium, all in the HF approximation. The lithium energy expression can be found in equation 58. In Table V, the expectation values of $\langle r^n \rangle$ for H^- and He using the wavefunctions tabulated above, ψ, the function $\psi_e = \exp(-kr(\beta+e^{-\frac{54}{dkr}}$ which is one of the best simple analytical representations of the HF wavefunction (three parameters), and the simple scaled function, $\psi_S = e^{-(Z-\frac{5}{16})r}$, are compared to the HF expectation values.

TABLE I

HARTREE-FOCK APPROXIMATIONS USING SIMPLE WAVEFUNCTIONS FOR SYSTEMS OF TWO TO SIX ELECTRONS

	$H^-(1^1S)$	$He(1^1S)$	$Li(^2S)^a$	$Li(^2S)^b$	$Be(^1S)$	$B(^2P)$	$C(^3P)$	$C(^1D)$	$C(^1S)$
α_1	1.2864	1.8978	2.7374	2.7505	3.7402	4.6444	5.5870	5.5837	5.5871
n_1	1.0812	1.0201	1.0020	1.0048	1.0203	1.0107	1.0149	1.0227	1.0149
α_2			0.9288	0.9330	1.3490	1.6108	1.9824	2.0875	2.0239
n_2			2.4970	2.5017	2.4376	2.2984	2.2880	2.3578	2.3154
α_3						1.1393	1.4458	1.4447	1.3617
n_3						1.7128	1.6998	1.6937	1.6482
p	0.6915	0.8732	0.9319	0.9304	0.9220	0.9448	0.9435	0.9294	0.9431
-E	0.48733	2.86148	7.43225	7.43234	14.5702	24.5233	37.6739	37.6122	37.5270
$-E_{HF}$	0.48793	2.86168	7.43273	7.43273	14.5730	24.5291	37.6886	37.6313	37.5495
ΔE^d	1.23 [c]	0.70	0.64	0.52	1.92	2.36	3.90	5.07	5.99

a constrained to be orthogonal

b non-orthogonal

c reference 8. All other HF energies are to be found in reference 23.

d $\Delta E = 10^4 \dfrac{E_{HF} - E}{E_{HF}}$

TABLE II

THE THREE BASIS-FUNCTION LITHIUM CALCULATIONS

	HF	UHF_1	UHF_2	EHF[a]	EHF[b]	EHF[c]
α_1	2.7515	2.7548	2.7470	3.2797	3.2711	3.2649
α_2	2.3307	2.7386	2.7308	2.0902	2.0953	2.0679
α_3	0.8523	0.9235	0.9269	0.7093	0.6822	0.7393
n_1	1.0054	1.0046	1.0026	0.9965	0.9952	0.9882
n_2	0.9856	1.0046	1.0020	1.0000	1.0000	1.0009
n_3	2.2074	2.4755	2.5036	2.1495	2.0358	2.3335
$-\lambda$	5.4569	6.3199	6.4054	13.200	7.7078	
p	0.9288	0.9309	0.9338	0.9917	0.9912	1.0031
-E	7.43240	7.43235	7.43226	7.44521	7.44504	7.44512
$\langle S^2 \rangle$	3/4	0.75004	0.75002	3/4	3/4	3/4

TABLE II ($n_1 = 1$ and $n_2 = 1$)

α_1	2.7347	2.7400	2.7390	3.2889	3.2869	3.2982[d]
α_2	2.5397	2.7266	2.7289	2.0903	2.0957	2.0678
α_3	0.8790	0.9221	0.9250	0.7118	0.6849	0.6390
n_3	2.3471	2.4960	2.5036	2.1407	2.0537	2
$-\lambda$	5.9465	6.3879	6.4040	13.200	7.8011	
p	0.9341	0.9349	0.9343	0.9898	0.9895	1
-E	7.43223	7.43218	7.43217	7.44513	7.44494	7.4436
$\langle S^2 \rangle$	3/4	0.75002	0.75001	3/4	3/4	3/4
D(0)	14.376	14.350	14.375	13.727	13.739	
Q(0)	0.1647	0.2884	0.2627	0.2207	0.1858	
$\langle H_{CO} \rangle$	572[e]	1002	912	767	646	

TABLE II. Footnotes

a $\langle \chi_1/\chi_3 \rangle \neq 0$

b $\langle \chi_1/\chi_3 \rangle = 0$

c $\delta = 0$

d $\delta = 0$ see reference 50

e units of $\langle H_{CO} \rangle$ are Mc/sec

For the HF approximation, -E = 7.43273, D(0) = 13.827, Q(0) = 0.1666; ref. 23.

For the UHF approximation -E = 7.43275 and Q(0) = 0.2248; ref. 35.

For the EHF approximation, -E = 7.44748 and Q(0) = 0.1910; ref. 40.

For the EHF (G1 method), -E = 7.44756, D(0) = 13.864, Q(0) = 0.2095; ref. 42.

The experimental value of Q(0) is 0.2313 which leads to a hyperfine splitting of 805.512 Mc/sec.

TABLE III

THE EXCITED STATES AND THE EXTENDED HARTREE-FOCK CALCULATIONS FOR HELIUM

	2^3S	2^3S	2^3S[a]	1^1S	1^1S	2^1S[b]
α_1	2.0010	2.0033	2.0033	1.2368	1.2413	1.9425
n_1	0.9999	1.0004	1	1.0240	0.9868	0.9561
α_2					3.3691	2.2465
n_2					4.4401	1.1090
λ					0.1021	0.7292
α_1'	0.6917	1.8816	1.8815	2.1647	2.1356	1.0338
n_1	2.4856	1.0001	1	0.9841	0.9837	0.9203
α_2'		0.6868	0.6858		3.4705	0.6405
n_2'		2.4180	2.4149		1.2875	2.4518
λ'		-5.0777	-5.0645		0.0753	-4.0341
p	1.0016	0.9987	0.9986	0.9841	0.9916	0.9686
-E	2.17413	2.17422	2.17422	2.87602	2.87741	2.14330

a The hyperfine splitting for this wavefunction is 6751 mc/sec the contribution of the orbital $\chi_1 \backsim 1S$ to this splitting is 6531 Mc/sec. The theoretical value is 6739.84 Mc/sec[51] and the experimental value is 6739.71±0.05 Mc/sec.[52]

b For the case where this state is not orthogonal to the ground state, E = -2.15665 (experimentally E = -2.14598[53]); for the doubly constrained case E = -2.08572.

The various HF and EHF energies found in reference 48 are $E_{HF}(2^3S) = -2.17426$, $E_{EHF}(1^1S) = -2.87799$, and $E_{EHF}(2^1S) = -2.14347$.

TABLE IV

LITHIUM ATOM, HYDRIDE ION AND HELIUM ATOM
DOUBLE-PRECISION CALCULATIONS

	$Li(^2S)$	$H^-(1^1S)$	$He(1^1S)$
α_1	2.7790954	0.6153571	1.5366610
α_2	2.4574784	1.4030013	3.0734678
α_3	0.9092231		
n_1	1.0117796	0.9295687	0.9803386
n_2	0.9929810	1.1130452	1.0729370
n_3	2.3273439		
λ		0.4320158	0.1487237
p	0.9192757	0.8746764	0.9685718
-E	7.4325410	0.4879234	2.8616789
$-E_{HF}$	7.4327257[a]	0.48793[b]	2.8616799[c]

a reference 23

b reference 8

c reference 22

TABLE V

EXPECTATION VALUES OF $\langle r^n \rangle$ FOR THE DOUBLE-ZETA WAVEFUNCTIONS OF THE HYDRIDE ION AND THE HELIUM ATOM

The Hydride Ion

	Ψ_e	Ψ	Ψ_{HF}[a]	Ψ_s
$\langle r^{-2} \rangle$	1.0801	1.0815	1.0806	0.9453
$\langle r^{-1} \rangle$	0.6857	0.6857	0.6857	0.6874
$\langle r \rangle$	2.4999	2.5022	2.5039	2.1817
$\langle r^2 \rangle$	9.3210	9.3745	9.4105	6.3468
$\langle r^3 \rangle$	47.158	48.111	48.690	23.079
$\langle r^4 \rangle$	301.91	317.16	326.01	100.71

The Helium Atom

	Ψ_e	Ψ	Ψ_{HF}[b]	Ψ_s
$\langle r^{-2} \rangle$	5.9961	5.9955	5.9956	5.6953
$\langle r^{-1} \rangle$	1.6873	1.6873	1.6873	1.6875
$\langle r \rangle$	0.9272	0.9273	0.9273	0.8889
$\langle r^2 \rangle$	1.1840	1.1846	1.1848	1.0534
$\langle r^3 \rangle$	1.9354	1.9393	1.9406	1.5607
$\langle r^4 \rangle$	3.8604	3.8814	3.8879	2.7745

a the values in reference 55 are given in Rydberg units

b see reference 54

The energy values obtained from $\Psi_e(H^-)$ and $\Psi_e(He)$ are -0.4879108 and -2.8616732, respectively. The expectation values for $\langle 1/r_{12} \rangle$ using these double-zeta functions are 0.3955 and 1.0258 for H^- and He.

4. DISCUSSION

A. Approximations to Hartree-Fock Energies Using Simple Orbitals

This part of the discussion concerns itself with the calculations detailed in Table I. Let us consider some gross features of the calculations on the neutral atoms found therein. Systems of two to six electrons, involving orbitals formed from either a single basis function or a linear combination of basis functions whose coefficients are determined by Löwdin orthogonalization, are treated. However, it has been proven that determinants whose doubly occupied s-orbitals are formed by this orthogonalization scheme give the same energy as determinants whose s-orbitals are constructed from single basis functions. Therefore orbitals of the wavefunctions discussed here will be treated as simple single function forms.

Consider the quantity ΔE which expresses the deviation from the true HF energy. The reason for the highest accuracy in the lithium calculations and for the error in boron being much nearer in magnitude to the beryllium error rather than to the carbon calculation errors can simply be the ratio of basis functions used to electrons in the atoms; namely, 2, 1.5, 2, 1.6, 2 as the number of electrons goes

from two to six, respectively. It was thought that the oscillatory behavior of the p-parameter indicated a tendency towards a smaller dependence in the wavefunction upon this parameter as the ratio of basis functions to the number of electrons decreased. However, a closer look at the p-value of the ^1D wavefunction of carbon leads one to believe that there is a tendency towards smaller p-dependence in open-shell wavefunctions -- this, by the way, seems to justify the minimization of an apparently closed-shell determinant to obtain the open-shell ^1S wavefunction by projection. The smaller the p-parameter, the slower the electron distribution functions (wavefunctions) tail off. Hence the charge will be more diffuse in general.

In closed-shell wavefunctions there is a great probability for electrons of opposite spin to occupy the same space ($\langle \delta(r_{ij}) \rangle$-case of helium[56]). This would cause the energy to rise. A small p for closed-shell systems would tend to spread the charge, lessen the probability of such electronic encounters, and thereby lower the energy. The p value cannot; however, be made so small that the attractive potential energy suffers grieviously.

The energies realized by these functions worsen as the number of electrons increase. Because of their simplicity, the functions employed herein are less capable of rep-

resenting the true HF higher orbitals. It is also noted that orthogonality imposed on a two basis function lithium wavefunction is, indeed a constraint.

Let us investigate some screening factors for these orbitals. According to Slater,[57]

$$\phi = r^{n^*-1} e^{-Z_{n^*}/n^* r} Y_{l,m}(\theta,\phi) \tag{67}$$

where n* is the effective quantum number and Z_{n^*} is the effective charge. Replacing r^p by R and considering the unnormalized radial portion of a GETF,

$$\phi = R^{\frac{n-1}{p}} e^{-\alpha R} \tag{68}$$

it is easily seen that;

$$n^* = \frac{n-1}{p} + 1$$

and

$$Z_{n^*} = \alpha n^*. \tag{69}$$

The screening factor, S_i, will be defined as that fraction of the charge experienced by an electron in the i-th orbital:

$$S_i = \frac{\alpha_i}{Z}\left(\frac{n_i - 1 + p_i}{p_i}\right). \tag{70}$$

Here $S_i < 1$ denotes screening, $S_i = 1$; no screening and $S_i > 1$; "antiscreening". In this scheme α_i may be greater than Z, the nuclear charge, and still represent screening if n_i is

sufficiently smaller than 1. The screening factors are calculated for the orbitals of the systems under study and tabulated in Table VI.

One observes immediately a screening factor of greater than unity for the hydride ion. There is not much to be said here since the HF method predicts this ion to be unstable. The factors for the "2s" orbitals are smaller than those for the "1s" orbitals since the former are somewhat more screening than the latter because the maximum values of the "1s" orbitals lie closer to the nucleus than the maxima of the "2s" orbitals. The "2p" orbitals suffer the most screening since their maxima lie beyond the maxima of both s-orbitals. Since the screening factor varies inversely as the p-parameter, it is reasonable that the observed behavior - that the atoms containing only closed shells and subshells demonstrate a lesser degree of screening in their orbitals - occurs. If the role of a small p value is that of diffusing the electron charge distribution, the screening would, indeed, be diminished. Finally, Slater's constants are not applicable to GETF orbitals since these are charge independent and do not account for the penetration of the outer orbitals.

TABLE VI

SCREENING FACTORS FOR THE HARTREE-FOCK APPROXIMATIONS USING SIMPLE WAVEFUNCTIONS

	$H^-(1^1S)$	$He(1^1S)$	$Li(^2S)^a$	$Li(^2S)^b$	$Be(^1S)$
S_1	1.4038	0.9707	0.9145	0.9215	0.9570
S_2			0.8069	0.8130	0.8632

	$B(^2P)$	$C(^3P)$	$C(^1D)$	$C(^1S)$
S_1	0.9402	0.9470	0.9550	0.9458
S_2	0.7650	0.7814	0.8562	0.8078
S_3	0.3998	0.4198	0.4205	0.3830

a orthogonal

b non-orthogonal

B. The Three Basis-Function Lithium Calculations

The pertinent expressions concerning the three basis-function lithium calculations are to be found in equations 56 through 61, inclusively, and the final results are displayed in Table II.

It is known that the UHF method for lithium produces only a very slight improvement in the energy over the HF method, also, the UHF function is almost a pure doublet ($\langle \mathcal{S}^2 \rangle = 0.75001573$[35]). The second fact was observed. However, the UHF energies reported here are slightly worse than the displayed HF energies. There apparently is a restraint involved when the "2s" orbital is made somewhat dependent upon either the "1s" or the "1s'" orbitals, the former dependence being a bit more severe. In the core-polarized EHF method there is a great improvement in energy over the HF. Here, describing the "2s" orbital with two functions, though one be identical to the "1s" orbital, improves the energy a little over that obtained by a wavefunction whose "2s" orbital is defined by a single basis function, if strong orthogonality is not forced. The imposition of orthogonality between the "1s" and the "2s" orbitals of these approximate EHF functions raises the energy a little, since the orbitals are no longer fully optimized. It should be indicated that in more sophisticated numerical EHF methods orthogonality of the orbitals

does not constrain the wavefunction.[40,41] However, the G1 formulation of the EHF approximation which produces a better energy does poorly, admittedly, when orthogonality is imposed. This failure to realize a pleasing orthogonal orbital picture is dismissed by declaring such a representation to be unphysical.[42] The EHF procedure, in practice, is a recent development.

The investigations into hyperfine structure call attention to an important fact. If an orbital of s-symmetry be described by a linear combination of GETF's, all of the n parameters involved must be equal to or greater than unity with at least one of them equal to unity in order that an unphysical picture of zero or infinite charge density at the nucleus be not presented. One can still obtain good energies and other expectation values with wavefunctions upon which this restraint is not imposed. In this study, the energies obtained by forcing proper behavior at the nucleus are only slightly worse than those realized when this requirement is lifted. The spin densities for lithium are much smaller than the charge densities at the nucleus. This is expected since the core orbitals--much larger contributors to the charge density at the nucleus than the "2s" orbital--cancel their individual contributions almost completely due to antiparallel alignment of their spin vectors. The magnitude of the spin density at the nucleus is equal to the contribution

to the charge density at the nucleus for the "2s" orbital in the HF approximation since both core orbitals are identical. Comparison of the HF Q(O) value with the exact Q(O) value reveals that the outer orbital accounts for 70% of the spin density. In the UHF calculations, a great increase in spin densities over the HF value is observed, though these be almost perfect doublets and though the core orbitals differ only slightly. In fact, UHF_1 calculate a higher Q(O) than UHF_2 since the difference between α_1 and α_2 is greater in the former than it is in the latter. This sensitivity is expected since the individual spin densities of the core electrons are high (evidenced by a high charge density) and the contributions of the "1s" and "1s'" orbitals are made unequal without compensation. In the EHF method the two determinants D_1 and D_2 describe a situation where the α and β spins are averaged between the core orbitals, the increase in spin density thus arises from the interaction of the "2s" orbital with the unequal "1s" and "1s'" orbitals. Orthogonality in these simple cases eliminates the interaction between the outer orbital and the "1s" orbital, this is evidenced by a lowering of the spin density at the nucleus.

From these calculations one more important fact is brought to light; in these systems the lower the p value the higher the charge density at the nucleus. This could arise,

paradoxically, from the fact that, if the p parameter does, indeed, tend to spread out the charge distribution and separate the electrons, then the probability of finding one of them at the nucleus would increase.

C. The Excited States of Helium and the Helium EHF Calculations

The wavefunctions discussed in this part of the subsection are displayed in Table III. It is a necessary condition that the wavefunctions for the ground and all of the excited states of a system be mutually orthogonal. The 2^3S state presents no problem in this respect since it is already orthogonal to the 1^1S and 2^1S states because of spin. The 2^1S wavefunction was forced to be orthogonal to the 1^1S double-zeta HF function. Calculations were made using an excited singlet wavefunction whose orbitals were orthogonal but which was not orthogonal itself to the ground state. The resulting energy was unphysically low. The same wavefunction was later constrained to be orthogonal to the ground state. The energy realized; however, was poor since only four of the variable parameters could be adjusted. Finally, the tabulated 2^1S function is orthogonal to the 1^1S state wavefunction but does not contain orthogonal orbitals. The energy obtained from this function is very close to the given HF energy (the value is actually an EHF energy, HF is used in

the expanded meaning--either HF or EHF--in this reference[48]).

The triplet energy was calculated using an Eckart-like wavefunction (E_{Eckart} = -2.1639[58]); there was much improvement over this value. An extension of this scheme was contemplated where the wavefunction would resemble that of the 2^1S save for the sign between the determinants. It was found that λ_1 tended to zero and the orbitals tended to be orthogonal. Imposing the condition that the leading term in the s-orbital have an n parameter equal to unity was no restriction. There is excellent agreement with experiment in the hyperfine splitting, about 1/7 of one percent error. The charge density at the nucleus which is equal to twice the spin density is slightly overestimated and the p parameter is slightly less than unity. Unlike the case of the 2^3S state wavefunction, the extended Eckart wavefunction for the 1^1S state afforded only small improvement (E_{Eckart} = -2.8757[58] vs -2.8760). A wavefunction constructed from orbitals which were a linear combination of two basis functions was employed with a considerable improvement in the energy (0.00139 a.u.).

D. Wavefunctions Minimized by the Gradient Method

The wavefunctions discussed are to be found in Table IV.

The three basis-function lithium HF approximate wavefunction calculation was redone in double precision using a

method which utilizes the derivatives of the energy expression with respect to the variational parameters. These derivatives, components of a gradient vector, were found numerically. The definition of the partial derivative was utilized:

$$\frac{\partial E(\bar{\gamma})}{\partial \gamma_i} = \frac{E(\bar{\gamma}') - E(\bar{\gamma})}{h}$$

where $$\gamma_j' = \gamma_j + h\,\delta_{ij} \qquad (72)$$

Here $\bar{\gamma}$ and $\bar{\gamma}'$ are the set of variational parameters, γ_i and γ_i' are individual parameters and δ_{ij} is the Kronecker delta. For $h = 10^{-8}$ and the energy known to 16 or 17 places, the partial derivatives can be known to 7 or 8 places. The parameters found were significantly different and the energy was lowered 0.00014 a.u. below the corresponding single precision calculation.

An investigation of an extended double-zeta wavefunction for helium brought to light the deficiency of single precision arithmetic to treat the computation for such an accurate HF analytical approximation (energies slightly lower than the HF values were obtained). Therefore, it was decided that the double precision gradient minimization method be again employed; but this time the differentiations would be accomplished analytically (appendix III). The energy calculated differed trivially from the HF value (0.000001 a.u.).

It is interesting to note that the p parameters approach unity more closely in these and other two electron calculations than in their simpler counterparts; e.g., the Eckart ground state function vs the double-zeta split-shell function for the EHF helium approximation. This effect could merely stem from the very usage of more basis functions. It is observed that $\alpha_2 \lesssim 2\alpha_1$ (actually $\alpha_2 = 2.0000948\ \alpha_1$); this seems to be typical of many double-zeta helium calculations.[59] The expectation values for the hydride ion and the helium atom quoted in Table V approach the corresponding HF values very closely, more so than the unusual wavefunction, Ψ_e, which is designed to approximate the HF wavefunction. This at least demonstrates a similarity in behavior between these double-zeta functions and the HF wavefunctions at moderate r values. These wavefunctions depart from the HF functions markedly at zero and infinity. Consider the function defined in the following manner[17];

$$h(r) = -\frac{1}{2}\frac{d\ln\Psi^2}{dr}$$

manipulating, $h(r) = -\frac{1}{\Psi}\frac{d\Psi}{dr}$ (73)

At infinity this function takes on the value of 1.35495 and at the nucleus it is equal to 2.0; the cusping condition for helium. For these double-zeta function, h(r) dips below $h(\infty)_{HF}$ at about 60 a.u., but more distressingly, becomes infinite at r equal zero because of the appearance of n_1

smaller than unity in the wavefunction. These functions, despite this flaw, perform well since fulfillment of the virial theorem is much more important than having a correct cusp value.[54] Let,

$$V.T. = -\frac{\langle V_{op}\rangle}{\langle T_{op}\rangle} \tag{74}$$

where $\langle V_{op}\rangle$ and $\langle T_{op}\rangle$ are the average potential and kinetic energy, respectively. The virial theorem is satisfied for the potential operator in the Hamiltonian presented in Part I.A if V.T. = 2.[60] For helium V.T. = 1.9999999; for the hydride ion V.T. = 2.0.

E. The p Parameter and the Central Field Approximation

The great majority of the p parameters; except for the Eckart type helium triplet calculation and the simplest EHF lithium calculation, whose parameters are slightly higher than one, have a value of less than unity. It is known that HF wavefunctions converge slowly to zero as r approaches infinity.[17,54] This tailing effect can be approximated by $p < 1$. Since the independent particle model assumes that each electron moves in an averaged potential central field of the others, let us consider each orbital to satisfy the following equation.[29,40,41,42,57]

$$H_1\chi = \epsilon\chi$$

or

$$H_1'\chi = 0$$

where

$$H_1' = H_1 - \epsilon = -\tfrac{1}{2}\nabla^2 + U \tag{75}$$

Defining χ as a linear combination of basis functions,

$$H_1' \sum_k c_k \phi_k = 0 \tag{76}$$

In order that this equation hold for all values of the coordinates;

$$H_1' \phi_k = 0 \tag{77}$$

Let $$-\tfrac{1}{2} \nabla^2 \phi_k = -V_k$$

then $$\{U - V_k\} \phi_k = 0$$

therefore $$U = \sum_j V_j \delta_{jk}$$

where $$V_j = \{n_j(n_j-1) - l(l+1)\}/2r^2 - \alpha_j \rho (2n_j + \rho - 1)/r^{2-\rho} + \alpha_j^2 \rho^2 / r^{2-2\rho} \tag{78}$$

In order that V_j vanish or become a finite constant as r approaches infinity, p must be less than or equal to one. It can be expected that the use of simple gaussians to represent HF orbitals would yield poor results.[2,28]

The two exceptions to $\rho < 1$ share one common aspect; they have the form of an approximate EHF wavefunction where the "2s" orbital is represented by a single basis function (2^3S helium wavefunctions whose orbitals are non-orthogonal cannot be strictly considered as HF in nature). It can be indicated that for the EHF procedure on lithium, choosing hydrogenic 2s orbitals assures the quickest rate of conver-

gence.[40,41] It is not known what occurs in the case of initial 2s Slater orbitals. In the case under study it seems that not describing the "2s" orbitals adequately causes a breakdown of the independent particle model in these two calculations. However, this description is restored when two basis functions are used to construct the orbital.

SECTION III

GENERAL EXPONENTIAL TYPE FUNCTIONS AND ELECTRON CORRELATION

1. INTRODUCTION

In the independent particle models discussed in the last section, the detail of the way in which the electrons correlate their motions is not adequately represented. There are two basic methods of surpassing these approximations and including electron correlation: configuration interaction and introduction of interelectronic coordinates directly into the wavefunction. The first method is relatively simple, straightforward and easily adapted to many electron systems, but suffers the defect of slow convergence to the desired exact energy. The second method can guarantee very accurate results for two electron systems, but extension of the procedure to many electron calculations presents extreme computational difficulties.[61]

2. METHOD AND THEORY

A. Multiconfiguration Interaction

In the method of configuration interaction the total wavefunction, Ψ , is constructed from a linear combination of single configurations, Φ :

$$\Psi = \sum_k c_k \Phi_k \tag{79}$$

The energy may be expressed as;

$$E = \frac{\sum c_i c_j H_{ij}}{\sum c_i c_j S_{ij}}$$

where
$$H_{ij} = \langle \Phi_i | \mathcal{H} | \Phi_j \rangle \tag{80}$$
$$S_{ij} = \langle \Phi_i | \Phi_j \rangle$$

A well known condition that E be a minimum is,[62]

$$|H - \lambda S| = 0 \tag{81}$$

The desired energy is the lowest eigenvalue and the c_k are the components of its normalized eigenvector.

The proper term for the method employed in this paper is multiconfiguration interaction since all the non-linear parameters are varied whenever a new configuration is added.[4]

The formalism of multiconfiguration interaction will be utilized here only for the 1^1S state of the helium atom. Exploratory calculations on the radial limit and extensions of the Taylor-Parr wavefunction[5] will be considered.

The radial or S-limit of the Schrödinger equation is the solution of the spherical component of the Hamiltonian. This wavefunction would account for all of the radial correlation between the electrons. The Hamiltonian for the two electron atom is,

$$\mathcal{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \quad . \tag{82}$$

Let the electron expulsion be expressed as;

$$\frac{1}{r_{12}} = \sum_{l}^{\infty} \frac{r_<^l}{r_>^{l+1}} P_l(\cos\theta_{12}) \tag{83}$$

then the pertinent component of the Hamiltonian (l=0) is,

$$\mathcal{H} = -\frac{1}{2r_1^2}D_1 - \frac{1}{2r_2^2}D_2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_>} \tag{84}$$

where $r_>$ is the larger of r_1 and r_2[63] (see eq. 4 for D_i).

In practice the solution of this equation is approximated by extensive configuration interaction with determinants containing only s symmetry orbitals.[64] In this paper a wavefunction of four split-shell configurations was employed as well as a function of six closed-shell configurations. The split-shell configurations can be expressed as:

$$\Phi_k = |\Phi_k \bar{\Phi}_k'| + |\Phi_k' \bar{\Phi}_k|$$

with matrix elements,

$$\begin{aligned} H_{ij} = {} & (\phi_i|\phi_j)\langle\phi_i'|\phi_j'\rangle + (\phi_i'|\phi_j')\cdot \\ & \langle\phi_i|\phi_j\rangle + (\phi_i'|\phi_j)\langle\phi_i|\phi_j'\rangle + \\ & (\phi_i|\phi_j')\langle\phi_i'|\phi_j\rangle + (\phi_i\phi_j|\phi_i'\phi_j') \\ & + (\phi_i\phi_j'|\phi_i'\phi_j) \end{aligned} \tag{85}$$

$$S_{ij} = \langle\phi_i|\phi_j\rangle\langle\phi_i'|\phi_j'\rangle + \langle\phi_i'|\phi_j\rangle\langle\phi_i|\phi_j'\rangle$$

The closed-shell configurations can be expressed as;

$$\Phi_k = |\phi_k \bar{\phi}_k|$$

where
$$H_{ij} = 2(\phi_i|\phi_j)\langle\phi_i|\phi_j\rangle + (\phi_i\phi_j|\phi_i\phi_j) \quad (86)$$
$$S_{ij} = \langle\phi_i|\phi_j\rangle^2 .$$

The generalized Taylor-Parr wavefunction can be written in the following manner:

$$\Psi = \sum_{k=1}^{4} c_k \chi_k$$

here
$$\chi_k = |\phi_k \bar{\phi}'_k| + |\phi_k' \bar{\phi}_k| \quad (87)$$

Since the angular part of ϕ_k and ϕ_k' are the same the χ_k may be reformulated as;

$$\chi_k \{|R_k \bar{R}'_k| + |R_k' \bar{R}_k|\} O_0 Y_{k-1,0}(1) Y_{k-1,0}(2) \quad (88)$$

where R_k and R_k' are the radial parts of the orbitals.

If
$$O_0 = \prod_{l=1}^{k(k-1)} \left\{ 1 - \frac{\alpha^2}{l(l+1)} \right\} \quad (89)$$

then
$$O_0 Y_{k-1,0}(1) Y_{k-1,0}(2) = \frac{1}{\sqrt{k(k-1)}} \sum_{q=1}^{k(k-1)} (-1)^{q+1} \cdot Y_{k-1,k-q}(1) Y_{k-1,q-k}(2) .$$

is the expanded form of the angular part of the configuration, χ_k.[65] The matrix elements are of the form;

$$H_{ii} = (\phi_i|\phi_i) + 2(\phi_i|\phi_i')\langle\phi_i|\phi_i'\rangle + (\phi_i'|\phi_i') + (\phi_i\phi_i|\phi_i'\phi_i') + (\phi_i\phi_i'|\phi_i'\phi_i)$$

$$H_{ij} = (\phi_i \phi_j | \phi_i' \phi_j') + (\phi_i \phi_j' | \phi_i' \phi_j)$$

$$S_{ii} = 1 + \langle \phi_i | \phi_i' \rangle^2$$

$$S_{ij} = 0$$

(90)

The two electron integrations require constants other than a simple product of Clebsch-Gordon coefficients[29] as found in equation 4 of appendix II. These are displayed in Table VII.

In the Taylor-Parr function proper only the S-configuration is split. An extension wherein non-integral quantum numbers appear was proposed by Snyder.[66] The first angular term in the generalized function is a split P-configuration. This nomenclature should not be confused with the SPO (split-p-orbital) method which assumes the electrons to be correlated in such a manner that they spend most of their time in the different lobes.[68,69] In conclusion, one may think of the Taylor-Parr wavefunction as an approximate solution to the F-limit Schrödinger equation:

$$H = h_1 + h_2 + \sum_{k=0}^{3} \sum_{m=-k}^{k} \frac{4\pi}{2k+1} \frac{r_<^k}{r_>^{k+1}} Y^*_{k,|m|}(\theta_1, \phi_1) \cdot Y_{k,|m|}(\theta_2, \phi_2) . \quad (91)$$

TABLE VII

ANGULAR INTEGRATION COEFFICIENTS FOR THE TAYLOR-PARR WAVEFUNCTION

$l_1 + l_2$ even

k	0	2	4	6
ss	1			
sd	0	$1/5\sqrt{5}$		
pp	1	2/25		
pf	0	$9/25\sqrt{21}$	$4/27\sqrt{21}$	
ff	1	4/75	2/99	100/5577

$l_1 + l_2$ odd

k	1	3	5
sp	$1/3\sqrt{3}$		
sf	0	$1/7\sqrt{7}$	
pd	$2/3\sqrt{15}$	$9/49\sqrt{15}$	
df	$1/\sqrt{35}$	$4/21\sqrt{35}$	$100/726\sqrt{35}$

B. The Introduction of the Explicit Interelectronic Coordinate

It has been shown that even simple wavefunctions explicit in r_{12} demonstrate a marked improvement in energy.[56] The study of the following simple wavefunction in the Hylleraas coordinates u and s has been taken up:[7]

$$\psi = e^{-\frac{1}{2}s^p}(1 + cu^n) \tag{92}$$

where $s = r_1 + r_2$, $u = r_{12}$ and n is non-integral. The energy computed from this wavefunction may be written as

$$E = (k^2 T + kV)/N \tag{93}$$

where k is a scaling factor which is adjusted in such a manner that the virial theorem is satisfied.[70] Therefore,

$$\begin{aligned} k &= -\frac{V}{2T} \\ E &= -\frac{V^2}{4T} \\ \alpha &= \tfrac{1}{2}k^p \\ \text{and} \quad c' &= c\,k^n \end{aligned} \tag{94}$$

the quantity, α, may be regarded as an effective charge. The three integrals T, V and N are defined as:[71]

$$\begin{aligned} T &= 2\int_0^\infty ds \int_0^s du \int_0^u dt \{u(s^2-t^2)\cdot \\ &\quad \left[\left(\frac{\partial\psi}{\partial s}\right)^2 + \left(\frac{\partial\psi}{\partial t}\right)^2 + \left(\frac{\partial\psi}{\partial u}\right)^2\right] + 2s(u^2-t^2)\cdot \\ &\quad \frac{\partial\psi}{\partial s}\frac{\partial\psi}{\partial u} + 2t(s^2-u^2)\frac{\partial\psi}{\partial t}\frac{\partial\psi}{\partial u}\} \\ V &= \int_0^\infty ds \int_0^s du \int_0^u dt \left[4su - \frac{s^2-t^2}{2}\right]\psi^2 \\ N &= \frac{1}{8}\int_0^\infty ds \int_0^s du \int_0^u dt\, u(s^2-t^2)\psi^2 \end{aligned} \tag{95}$$

These are known as the kinetic energy, potential energy and normalization integrals, respectively. Evaluating these:

$$T = \frac{4}{30}\Gamma\left(\frac{4}{\rho}\right) + \frac{c}{6}\Gamma\left(\frac{4+n}{\rho}\right)\frac{(4+n)(n\rho - n^2 + 6\rho + 24)}{(3+n)(5+n)} + \frac{c^2}{3}\Gamma\left(\frac{4+2n}{\rho}\right)\left\{\frac{(4+2n+\rho)(2+n)(3+n)}{(5+2n)} - n(4+2n) + \frac{2n^2(2+n)}{1+2n}\right\}$$

$$V = -\frac{9}{4}\Gamma\left(\frac{5}{\rho}\right) - 2c\,\Gamma\left(\frac{5+n}{\rho}\right)\left(\frac{7n+13}{(2+n)(3+n)} + \frac{1}{3(4+n)}\right) - c^2\Gamma\left(\frac{5+2n}{\rho}\right)\left(\frac{14n+13}{2(1+n)(3+2n)} + \frac{1}{6(2+n)}\right) \quad (96)$$

$$N = \frac{1}{30}\Gamma\left(\frac{6}{\rho}\right) + \frac{c}{6}\Gamma\left(\frac{6+n}{\rho}\right) + \frac{c^2}{6}\Gamma\left(\frac{6+2n}{\rho}\right)\frac{3+n}{(3+2n)(5+2n)}$$

wavefunctions in the coordinates r_1, r_2 and r_{12} were studied for helium; these are of the form:

$$\Psi = \frac{1}{\sqrt{2}}\left\{|\phi_1(1)\bar{\phi}_2(2)| \pm |\phi_2(1)\bar{\phi}_1(2)|\right\}(1 + c r_{12}) \quad (97)$$

The plus sign defines the 1^1S state and the minus sign represents the 2^3S state wavefunctions. If the two orbitals are chosen to be identical then the closed-shell correlated singlet is signified. The Hamiltonian in the above mentioned coordinate system is

$$\mathcal{H} = -\frac{1}{2}\left\{\frac{1}{r_1^2}\frac{\partial}{\partial r_1}r_1^2\frac{\partial}{\partial r_1} + \frac{1}{r_2^2}\frac{\partial}{\partial r_2}r_2^2\frac{\partial}{\partial r_2} + \frac{2}{r_{12}^2}\frac{\partial}{\partial r_{12}}r_{12}^2\frac{\partial}{\partial r_{12}} + \frac{r_1^2 + r_{12}^2 - r_2^2}{r_1 r_{12}}\frac{\partial^2}{\partial r_1 \partial r_{12}} + \frac{r_2^2 + r_{12}^2 - r_1^2}{r_2 r_{12}}\frac{\partial^2}{\partial r_2 \partial r_{12}}\right\} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \quad (98)$$

The integrals are of the form

$$I = \int_0^\infty F_1(r_1) r_1 dr_1 \int_0^\infty F_2(r_2) r_2 dr_2 \cdot \int_{|r_2-r_1|}^{r_2+r_1} \frac{1}{2} r_{12}^{\nu+1} dr_{12}$$

where $$F_k(r_k) = r_k^{n_i+n_j-2+b_K} e^{-(a_i+a_j)r_k^p} \qquad (99)$$

here ν is (-1, 0, 1, 2) and b_k is dictated by the operation on electron k. The GETF's in this subsection are taken to be unnormalized. According to Perkins[72],

$$I = \int_0^\infty F_1(r_1) r_1^2 dr_1 \int_0^\infty F_2(r_2) r_2^2 dr_2 \cdot \sum_{k=0}^{[\frac{\nu+1}{2}]} C_\nu^k \frac{r_<^{2k}}{r_>^{\nu-2k}}$$

where $$C_\nu = \left(\frac{(2\nu+2)!}{(2k+1)!(2\nu-2k+1)!}\right)\frac{1}{\nu+2} \qquad (100)$$

here $[\frac{\nu+1}{2}]$ means the lesser of the integers close to $\frac{\nu+1}{2}$ if this expression is itself non-integral. For ν odd

$$I = \sum_{k=0}^{\frac{\nu+1}{2}} C_\nu^k \left[\int_0^\infty F_1(r_1) r_1^{2+2k} dr_1 \int_{r_1}^\infty F_2(r_2) r_2^{2+\nu-2k} dr_2 + \int_0^\infty F_2(r_2) r_2^{2+2k} dr_2 \int_{r_2}^\infty F_1(r_1) r_1^{2+\nu-2k} dr_1 \right]$$

ν even $$I = \sum_{k=0}^{\frac{\nu}{2}} C_\nu^k \int_0^\infty F_1(r_1) r_1^{2+2k} dr_1 \int_0^\infty F_2(r_2) r_2^{2+\nu-2k} dr_2 \qquad (101)$$

If one defines $F_1(r_1)$ as $\phi_i\phi_j r_1^{b_1}$ and $F_2(r_2)$ as $\phi_k\phi_l r_2^{b_2}$, one can express these integrals as;[1]

$$(\nu \text{ odd})\ I = \sum_{k=0}^{\frac{\nu+1}{2}} C_\nu^k \left[I_{X_1}(a_1, d_2) \frac{\Gamma(a_1)\,\Gamma(d_2)}{(d_i+d_j)^{a_1}(a_k+a_l)^{d_2}} + I_{X_2}(a_2, d_1) \frac{\Gamma(a_2)\,\Gamma(d_1)}{(a_k+a_l)^{a_2}(d_i+d_j)^{d_1}} \right] \frac{1}{\rho^2}$$

$$(\nu \text{ even})\ I = \sum_{k=0}^{\frac{\nu}{2}} C_\nu^k \frac{\Gamma(a_1)\,\Gamma(d_2)}{\rho^2 (d_i+d_j)^{a_1}(d_k+d_l)^{d_2}} \qquad (102)$$

here
$$a_1 = (n_i + n_j + b_1 + 1 + 2k)/\rho$$
$$a_2 = (n_k + n_l + b_2 + 1 + 2k)/\rho$$
$$d_1 = (n_i + n_j + b_1 + 1 - 2k + \nu)/\rho$$
$$d_2 = (n_k + n_l + b_2 + 1 - 2k + \nu)/\rho$$
$$X_1 = (d_i + d_j)/(d_i + d_j + d_k + d_l)$$
$$X_2 = (d_k + d_l)/(d_i + d_j + d_k + d_l)$$

Here $\Gamma(X)$ and $I_X(a,b)$ are the well-known gamma function and the incomplete beta function ratio.[73] Defining

$$G(i,j,m) = \frac{\Gamma\left(\frac{n_i + n_j - 3 + m}{\rho}\right)}{(d_i + d_j)^{\frac{n_i + n_j - 3 + m}{\rho}}}$$

and $F(i,j,m,q) = G(i,j,m+q)\,G(k,l,6-q)\,I_X(a,b)$ for even q

and $F(i,j,m,q) = G(i,j,m+q)\,G(k,l,6-q)\,I_{1-X}(b,a)$ for odd q

where $X = \dfrac{d_i + d_j}{2(d_1 + d_2)}$

$$a = (n_i + n_j - 3 + m + q)/\rho$$
$$b = (n_k + n_l + 3 - q)/\rho$$

(103)

one may write the energy expression as

$$E = \sum_{i,j}^{2} (T_{ij} + V_{ij} + B_{ij}) \Big/ \sum_{i,j}^{2} S_{ij} \qquad (104)$$

where

$$T_{ij} = -(a_i+a_j)^{-2}\{G(i,j,2)\,G(k,l,4)\,(A-B-a_i a_j(p-1)(n_i+n_j-1)) + 2C\,(\tfrac{1}{3}F(i,j,1,0)\cdot(A-2B-a_i a_j[2(1-p)+(p-2)(n_i+n_j)]+a_i^2+a_j^2) + F(i,j,1,1)(A-B-a_i a_j(p-1)\cdot(n_i+n_j-1)) + F(i,j,1,2)(A-a_i a_j\,p(p-1)\cdot(n_i+n_j)) + \tfrac{1}{3}F(i,j,1,3)(A+B-a_i a_j\cdot(p-1+(p+1)(n_i+n_j))+a_i^2+a_j^2)) + C^2\cdot(G(i,j,4)\,G(k,l,4)(A+B-a_i a_j(p+1)\cdot(n_i+n_j+1)) + G(i,j,2)\,G(k,l,6)\cdot(A-B-a_i a_j(p-1)(n_i+n_j-1)))\}$$

$$A = (a_i n_j - a_j n_i)^2 \;;\; B = a_i^2 n_j + a_j^2 n_i$$

$$V_{ij} = -2Z\{G(i,j,3)\,G(k,l,4) + 2C\,(F(i,j,2,1)+F(i,j,2,2)+\tfrac{1}{3}F(i,j,2,3)+\tfrac{1}{3}F(i,j,2,0)) + C^2(G(i,j,5)\,G(k,l,4)+G(i,j,3)\,G(k,l,6))\}$$

$$R_{ij} = F(i,j,1,3)+F(i,j,1,2)+2C\,G(i,j,4)\,G(k,l,4) + C^2(F(i,j,3,1)+F(i,j,3,2)+\tfrac{1}{3}F(i,j,3,3)+\tfrac{1}{3}F(i,j,3,0))$$

$$S_{ij} = G(i,j,4)\,G(k,l,4)+2C\,(F(i,j,3,1)+F(i,j,3,2)+\tfrac{1}{3}F(i,j,3,3)+\tfrac{1}{3}F(i,j,3,0)) + C^2(G(i,j,6)\,G(k,l,4)+G(i,j,4)\,G(k,l,6))$$

where T_{ij}, V_{ij}, R_{ij}, and S_{ij} are components of the kinetic energy integral, the electron-nucleus potential energy integral, the electron repulsion energy integral and the overlap integral, respectively. Here, k = 3-i and l = 3-j.

3. RESULTS

The set of tables presented in this segment of the paper display pertinent final results of the multiconfiguration interaction and the explicit electron correlation calculations. The first three tables, VIII, IX, and X, contain the parameters of the four term split-shell S wavefunction and the six configuration closed-shell S-wavefunction, the matrix elements H_{ij} and S_{ij} between the configurations of these wavefunctions, and the energies and p values for the stepwise build-up of these functions, respectively. The extensions of the Taylor-Parr wavefunction considered are this function with variable n quantum numbers, this function with both variable n and variable p, and the last extension wherein the angular configurations are split-shelled. Tables XI, XII, and XIII display the parameters, the matrix elements, and the energy build-up and angular configuration energy increment, respectively, for the Taylor-Parr wavefunction and its extensions. Tables XIV and XV contain information on the wavefunctions which include r_{12} explicitly. The first table deals with the function in the Hylleraas coordinates.

TABLE VIII

PARAMETERS FOR THE S-WAVEFUNCTIONS

The Four Term Split-Shell Function

N	α_N	n_N	α'_N	n'_N	C_N
1	1.2641	0.9965	2.0825	0.9949	0.97932
2	2.0429	2.0000	2.2259	1.0406	-0.18516
3	3.6179	2.0000	4.1215	2.3000	-0.06239
4	4.0774	4.0010	4.1140	4.0000	-0.05249

p = 1.0026

The Six Term Closed-Shell Function

N	α_N	n_N	C_N
1	1.4862	0.9957	0.97772
2	1.8229	2.2123	-0.19659
3	4.1698	2.5263	-0.03956
4	2.8876	2.9234	-0.03539
5	8.0974	8.0750	-0.04123
6	9.0006	9.0000	-0.02996

p = 0.9740

TABLE IX

THE MATRIX ELEMENTS FOR THE S-WAVEFUNCTIONS

The Four Term Split-Shell Function

	1	2	3	4
1	-2.87309	-2.84458	-2.44892	-2.24666
2		-2.76261	-2.25919	-2.19231
3			-1.33739	-1.67416
4				-0.86737
1	1	0.99140	0.87413	0.80154
2		1	0.86247	0.85138
3			1	0.65711
4				1

The first group of matrix elements are the H_{ij}, the second group; the S_{ij}

The Six Term Closed-Shell Function

	1	2	3	4	5	6
1	-2.80136	-2.05829	-2.31908	-2.25441	-1.69474	-1.62869
2		-1.70484	-1.28672	-1.56679	-0.95172	-0.89879
3			-1.18599	-1.51444	-1.50234	-1.49386
4				-1.50472	-0.78551	-0.72491
5					0.93720	1.13237
6						1.35540
1	1	0.81597	0.84289	0.88819	0.69780	0.67233
2		1	0.48025	0.91718	0.67528	0.65060
3			1	0.67087	0.61828	0.59968
4				1	0.87246	0.84981
5					1	0.99860
6						1

The first group of matrix elements are the H_{ij}, the second; the S_{ij}

TABLE X

THE COMPARISON OF THE BUILD-UP OF THE S-WAVEFUNCTIONS WITH THE HANDLER-JOY FOUR TERM WAVEFUNCTION

	1	2	3	4	5	6
E^a	-2.86148	-2.87693	-2.78851	-2.87876	-2.87882	-2.87887
p	0.8732	0.9125	0.9647	0.9647	0.9700	0.9740
E^b	-2.87602	-2.87810	-2.87874	-2.87886		
p	0.9841	1.0854	0.9915	1.0026		
E^c	-2.87566	-2.87773	-2.87866	-2.87889		

a the closed-shell expansion

b the split-shell expansion

c the Handler-Joy wavefunction to four terms[6]

The exact radial limit is taken to be $-2.8790280 \pm 1.8 \times 10^{-6}$.[74]

TABLE XI

THE PARAMETERS FOR THE TAYLOR-PARR WAVEFUNCTION AND ITS EXTENSIONS

	a	b	c	d
α_1	1.2016	1.2239	1.2307	1.2450
n_1	1.0	1.0170	1.0200	1.0223
α'_1	2.1762	2.1390	2.1409	2.1524
n'_1	1.0	0.9801	0.9800	0.9834
α_2	2.4830	2.7651	2.7653	2.5123
n_2	2.0	2.2467	2.2368	2.0300
α'_2				3.0526
n'_2				2.4528
α_3	3.6298	4.2247	4.0927	3.6843
n_3	3.0	3.5391	3.3929	3.0300
α'_3				4.6880
n'_3				3.8150
α_4	4.7700	5.2711	5.1170	4.9001
n_4	4.0	4.4046	4.3000	4.0000
α'_4				5.0680
n'_4				4.0300
c_1	0.99810	0.99808	0.99809	0.99808
c_2	-0.06021	-0.06058	-0.06047	-0.06059
c_3	-0.01205	-0.01214	-0.01207	-0.01198
c_4	-0.00431	-0.00427	-0.00430	-0.00415
E	-2.89749	-2.89795	-2.89797	-2.89799

a the Taylor-Parr wavefunction

b the Taylor-Parr wavefunction with non-integral n

c the Taylor-Parr wavefunction with non-intregal n and variable p

d the function described in c but with split angular configurations

TABLE XII

THE MATRIX ELEMENTS FOR THE TAYLOR-PARR WAVEFUNCTION AND ITS EXTENSIONS

		1	2	3	4
1	a	-2.87561	0.318556	0.178520	0.117800
	b	-2.87588	0.319520	0.178176	0.119018
	c	-2.87589	0.320238	0.179291	0.118235
	d	-2.87593	0.319459	0.180285	0.121360
2	a		2.27572	0.439814	0.273456
	b		2.25555	0.423345	0.284161
	c		2.27669	0.453766	0.282458
	d		2.25515	0.453772	0.283458
3	a			9.50596	0.506924
	b			9.30761	0.525733
	c			9.46863	0.521456
	d			9.64271	0.526855
4	a				19.2120
	b				19.4107
	c				19.0931
	d				20.6502

a the Taylor-Parr wavefunction

b the Taylor-Parr wavefunction non-integral n

c the Taylor-Parr wavefunction non-integral n, and variable p

d the function described in c but with split angular configurations

TABLE XIII

THE ENERGY BUILD-UP AND ANGULAR CONFIGURATION ENERGY INCREMENTS FOR THE TAYLOR-PARR WAVEFUNCTIONS AND ITS EXTENSIONS

The Energy Build-up for the Taylor-Parr Wavefunctions and P-Values

	1	2	3	4
E^a	-2.87566	-2.89523	-2.89708	-2.89742
E^b	-2.87568	-2.89570	-2.89754	-2.89795
E^c	-2.87602	-2.89574	-2.89759	-2.89797
p	0.9841	0.9901	0.9896	0.9983
E^d	-2.87602	-2.89575	-2.89760	-2.89799
p	0.9841	0.9891	0.9898	0.9918

The Angular Configuration Energy Contributions

	a	b	c	d	e
P	-0.01957	-0.01982	-0.01972	-0.01973	-0.02140
D	-0.00185	-0.00184	-0.00185	-0.00185	-0.00228
F	-0.00041	-0.00041	-0.00038	-0.00039	-0.00055

a the Taylor-Parr wavefunction

b the Taylor-Parr wavefunction non-integral n

c the Taylor-Parr wavefunction non-integral n and variable p

d the function described in c but with the angular configurations split

e suggested limit[75]

TABLE XIV

THE PARAMETERS FOR THE WAVEFUNCTION IN THE VARIABLES s AND u

p	1.0	1.0	0.9776	0.9691
n	1.0	0.9826	1.0	0.9430
c'	0.3658	0.3717	0.3751	0.3981
α	1.8497	1.8484	1.9161	1.9371
E	-2.89112	-2.89115	-2.89147	-2.89162

TABLE XV

PARAMETERS FOR THE WAVEFUNCTIONS IN THE COORDINATES r_1, r_2, and r_{12}

	1^1S^a	1^1S	1^1S^a	1^1S	2^3S
α_1	1.8497	1.9593	2.208	2.2017	2.0542
n_1	1.0	1.0088	1.0	1.0041	1.0132
α_2			1.436	1.4433	0.8198
n_2			1.0	0.9791	2.6428
c	0.3658	0.3445	0.2924	0.2943	0.0433
p	1.0	0.9261	1.0	0.9902	0.9787
E	-2.89112	-2.89764	-2.90142	-2.90171	-2.17462

a see reference 8

The exact energy for 1^1S helium is -2.90372[76] for the 2^3S state it is -2.17523.[77]

Here this function with certain restraints imposed upon the various parameters as well as the unconstrained wavefunction is displayed. The reader should be reminded that the α value in this table is not a variational parameter. The second table contains the closed-shell and the split-shell 1^1S state and the 2^3S state correlated helium calculations.

4. DISCUSSION

It shall be demonstrated that for GETF's where p is the same for all configurations this formalism fails to realize any great improvement in energy over simpler forms. On considering the split-shell four term radial function, one is struck by the blatant fact that the simpler corresponding Handler-Joy wavefunction produces a slightly better energy. Two factors could have contributed to this reverse. The presumably more important of these is the extreme convolution of the energy surface.[6] Many runs were executed for this particular case; but one was somewhat stifled by the ignorance of the Handler-Joy parameters for the optimized four term wavefunction. The second factor was the utilization of single precision matrix diagonalization routines. Whether the calculations were affected adversely or favorably is not known. Mindful that non-integral quantum numbers usually do not speed up the convergence for many-termed wavefunctions to an appreciable degree[6,78], one concludes

that this function would probably have not been better than the reference wavefunction had the true optimum parameters been found. The incremental improvement in energy as one adds configurations to the wavefunction in question is -0.00208, -0.00064 and -0.00012 a.u., on the other hand, the reference wavefunction increments as -0.00207, -0.00093 and -0.00023 for the introduction of the second, third and fourth terms, respectively. The third configuration must necessarily improve the energy to a smaller degree than the corresponding term of the Handler-Joy function less the radial limit be exceeded. It seems that great improvement in the first configuration for these functions entails inferior improvement in the subsequent terms. In the closed-shell case there seems to be rapid convergence until the p value stabilizes (slowly increasing) in the third configuration, thereafter additional terms contribute little to the energy.

The generalization of the Taylor-Parr wavefunction produced similar unspectacular results. For the simple case of n, integral and p equal to one, splitting of the angular configurations does not lower the energy. For the extended case, n and p continuously variable, this splitting improved the energy minutely. This residual in-out correlation could probably be eliminated from the angular terms if a better

radial configuration were used or if multiple radial terms were employed. From the results exposed in the latter portion of Table XIII, varying the p parameter apparently allows the angular configurations to contribute less to the total energy. The magnitude of this parameter could be governed more or less by the first term which may improve itself at the expense of the others. This inequity could probably be alleviated by allowing each configuration to control its own p parameter. However, the integrations between the configurations would now have to be performed numerically since suitable analytical expressions for these integrals are presently not available.

GETF's as employed in the wavefunctions displayed in Tables XIV and XV are not amenable to dramatic energy improvements. The first function employed evinces little amelioration over the simpler form $e^{-\frac{1}{2}s}(1+cu)$ as p and n are varied. There is a general trend in this wavefunction toward increasing c and apparent charge, α, as the energy improves. The next forms under study can be thought of as restricted two-configuration wavefunctions of the type $f(r_1,r_2)+cr_{12}f(r_1,r_2)$. Similarly to the various multiconfiguration wavefunctions, one can expect a heavy dependence upon the first term; that is, the more energy accounted for

by a wavefunction of a single configuration the less energy contributed by successive configurations. To discuss these wavefunctions properly then, one should consider their uncorrelated counterparts.

The increment in energy of the correlated closed-shell functions over the non-correlated corresponding wavefunctions for p and n fixed; and p and n variable are -0.04346 and -0.03616 a.u., respectively. It seems that the inclusion of the coordinate r_{12} in the first case aids in the recovery of some of the non-correlation energy since the single configuration wavefunction produces an energy widely departing from that of the HF. The split-shell wavefunctions are less improved by the introduction of the interelectronic coordinate since they already assume some radial correlation. The energy lowering due to the inclusion of r_{12} is -0.02576 and -0.02569 a.u., respectively for the Eckart function analog and the related variable n and p wavefunction. The effect due to such correlation is about the same in both cases. Correlation improves the triplet energy by -0.00049 a.u., a recovery of about 45% of the remaining energy between the non-correlated triplet function energy and the exact energy.

It is noticed that the p values for the singlet cases increased but those for the triplet cases decreased with respect to the p parameters in their non-correlated

counterparts. According to the findings in the previous section, a lower p value was accompanied by a raising of the charge density at the nucleus. Comparing fairly accurate calculations containing and excluding the variable r_{12},[49,56,77] it was found that the charge density at the nucleus is raised for the singlet state but lowered for the triplet state. If the interpretation for the p value in regards to behavior at the nucleus as given in section II is assumed, the opposite is predicted here. The relationship, if any, between p and the variable r_{12} is not known. A higher p value would predict a lesser magnitude for $\langle \delta(r_{12}) \rangle$, this is observed in the singlet state.[56] But $\langle \delta(r_{12}) \rangle$ for the triplet is automatically zero due to the antisymmetry of the spatial part of the wavefunction.

SECTION IV

SUMMARY

Single configuration wavefunctions are, in the main, greatly improved by the usage of GETF's as a basis set. If behavior at the nucleus is to be faithfully reproduced, the p variable assumes an important role since now all the n's cannot be defined as continuous variables. The scheme employed, one p the same for all basis functions, renders these slightly more interdependent. This seems to prevent the reproduction of notably better energies over cases when wavefunctions of many configurations are considered. Much work has been expended on functions involving different p's; but no analytical solutions which converge at a reasonable rate have been found for the integrations. Numerical methods might be promising since integrals containing functions of different p values can be transformed in such a fashion that the integrand is a smooth monotonically decreasing function with a maximum value of unity at r = 0 and an asymptote of zero.

The minimization for the most part is a variation of the direct search method[79] according to Chandler.[80] For most non-linear problems it is purported to be far superior to the methods of steepest descent, Newton-Gauss iteration,

conjugate directions, parallel tangents, and the like. This method, as do most of the others, guarantees only a local minimum. Thus the choice of initial parameters is important. In the formalism of the GETF's here employed, the energy expressions are pervaded with the parameter, p. This type of expression is most unusual in the realm of non-linear equations encountered in this particular segment of quantum mechanical calculations. When many parameters α_i and n_i are involved, the choice of p must be judicious since it changes little during the optimization procedure. This situation of relative inflexibility might not exist had each basis function its own p parameter. For the three double precision calculations mentioned in this paper, a variation of the Davidon method[11,81] which incorporates both conjugate directions and steepest descents, was employed with favorable results. Full endorsement cannot yet be given to this procedure since the maximum number of variables encountered was seven and since the runs utilizing the Chandler routine were computed in single precision arithmetic.

A relationship between the energy improvement during minimization and changes in certain variables was sought so that the procedure may be programmed more efficiently. After inserting initial parameters in different orders; selectively minimizing with respect to some while masking others; and extensively studying trace maps of the optimization process,

it was concluded that for reasonably chosen parameters there is no correlation between energy improvement during optimization and variations in certain parameters. However, it was found that the use of $\tilde{\alpha}_i = \frac{\alpha_i}{\bar{n}_i}$ and $\tilde{n}_i = \frac{n_i}{\rho}$ was slightly more efficient then the use of n_i and α_i as parameters in the minimization procedure.

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APPENDIX I

THE GENERAL EXPONENTIAL TYPE FUNCTIONS

The explicit form of these basis functions can be found in equation 9. Let us consider the radial part of the unnormalized function; namely,

$$\Phi = r^{n-1} e^{-\alpha r^{\rho}} \tag{1}$$

Three important facts about this function are interesting; the value at r = 0, which aids to determine the properties of an atomic system at the nucleus, the value r_{max}, where the function has its maximum, which determines the property of peaking; the value of the function at large r, which determines tailing, which is of great importance in Hartree-Fock approximate wavefunctions. At the nucleus the most important parameter is n. If n is smaller than one, the function assumes an infinite magnitude; for n equal to one the function is unity; for n greater than one the function vanishes at the nucleus, The first case has no physical significance, the second case is necessary for at least one of the terms in an orbital of s-symmetry. The maximum of the function is determined to be;

$$r_{max} = \left(\frac{n-1}{\alpha\rho}\right)^{\frac{1}{\rho}} \tag{2}$$

For n smaller than one there is a singularity at the nucleus, r_{max} increases as n increases but decreases as α increases if n is greater than one. The parameter p also affects r_{max} only when n is larger than unity. The manner in which r_{max} changes with p is more complex than the variation with respect to α and n. Let us first take an extremum value of r_{max} with respect to p:

when $$\frac{\partial r_{max}}{\partial \rho} = 0$$

then $$\rho_{ext} = \frac{n-1}{\alpha}$$

and $$\left[\frac{\partial^2 r_{max}}{\partial \rho^2}\right]_{\rho_{ext}} = \frac{1}{\rho_{ext}^3} e^{-\frac{1}{\rho_{ext}}} \qquad (3)$$

Since the second partial derivative is positive, $P_{ext} = P_{min}$, signifying a minimum in r_{max}. Hence r_{max} decreases as p approaches p_{min} from either the right or the left. All three parameters have some control over tailing. The function tails off more slowly if α decreases or p decreases or n increases. Let us attempt to discern the relative importance of these parameters with respect to this property. A tailing factor for the parameters (α, n, p) will be defined as:

$$F_\gamma = \ln \frac{\phi_1}{\phi_2} \qquad (4)$$

where ϕ_2 decreases faster than ϕ_1 as r approaches infinity. These functions have all parameters in common except for γ_1 and γ_2.

$$F_\alpha = (\alpha_2 - \alpha_1) r^{p_2}$$
$$F_p = \alpha_1 (r^{p_2} - r^{p_1})$$
$$F_n = (n_1 - n_2) \ln r \qquad (5)$$

One can appreciate the tailing off contribution of p a little more if it is born in mind that α must describe something that resembles an effective charge. At very large distances, n would have a miniscule effect on tailing compared to α and p, since F_n increases as the log of r, whilst F and F_p increase as a power of r. If all the parameters in ϕ_1 and ϕ_2 differ, the following tailing factor may be ascribed;

$$F_T = F_n + F_\alpha + F_p \qquad (6)$$

In this case some of the F_γ might be negative.

There follow three diagrams. Figure I depicts the tailing properties of p. Here α is constant, n is one and p assumes the values, greater than one, one, and less than one. Figure II illustrates all the properties of n. In this graph α and p are held constant while n takes on values less than, greater than, and equal to unity. The last figure represents functions with differing α but equal n and p.

FIGURE I

THE p PARAMETER

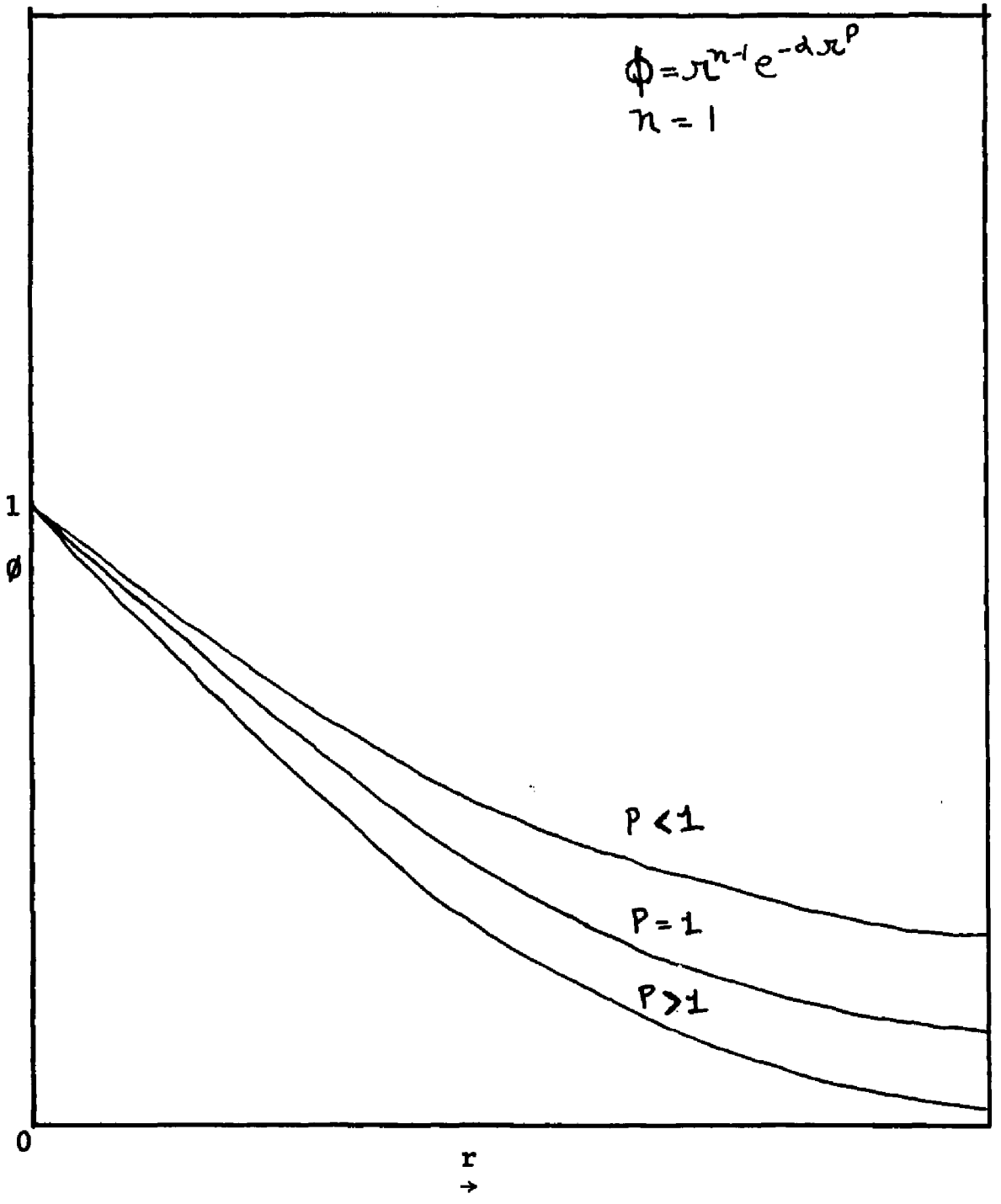


FIGURE II

THE n PARAMETER

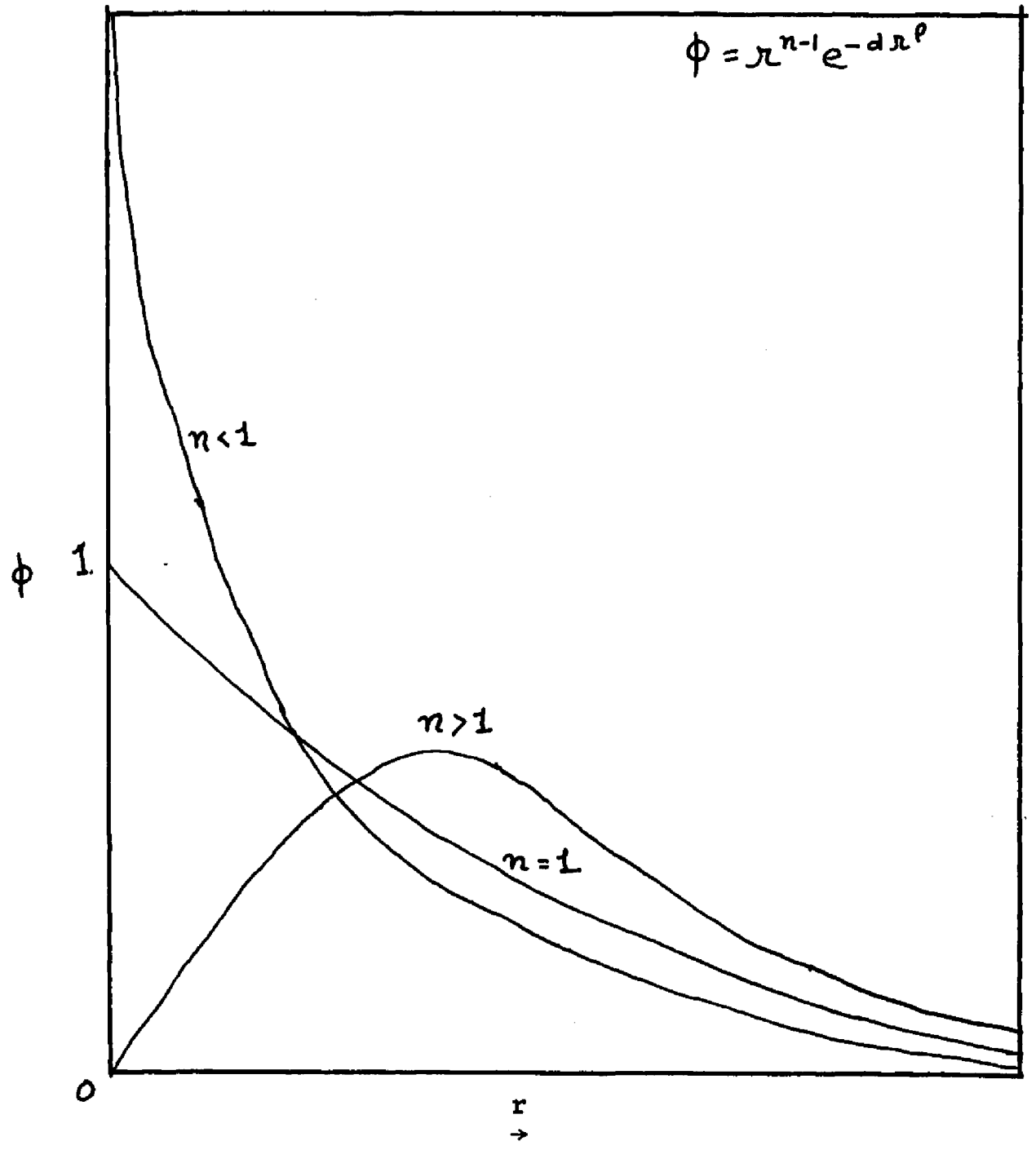
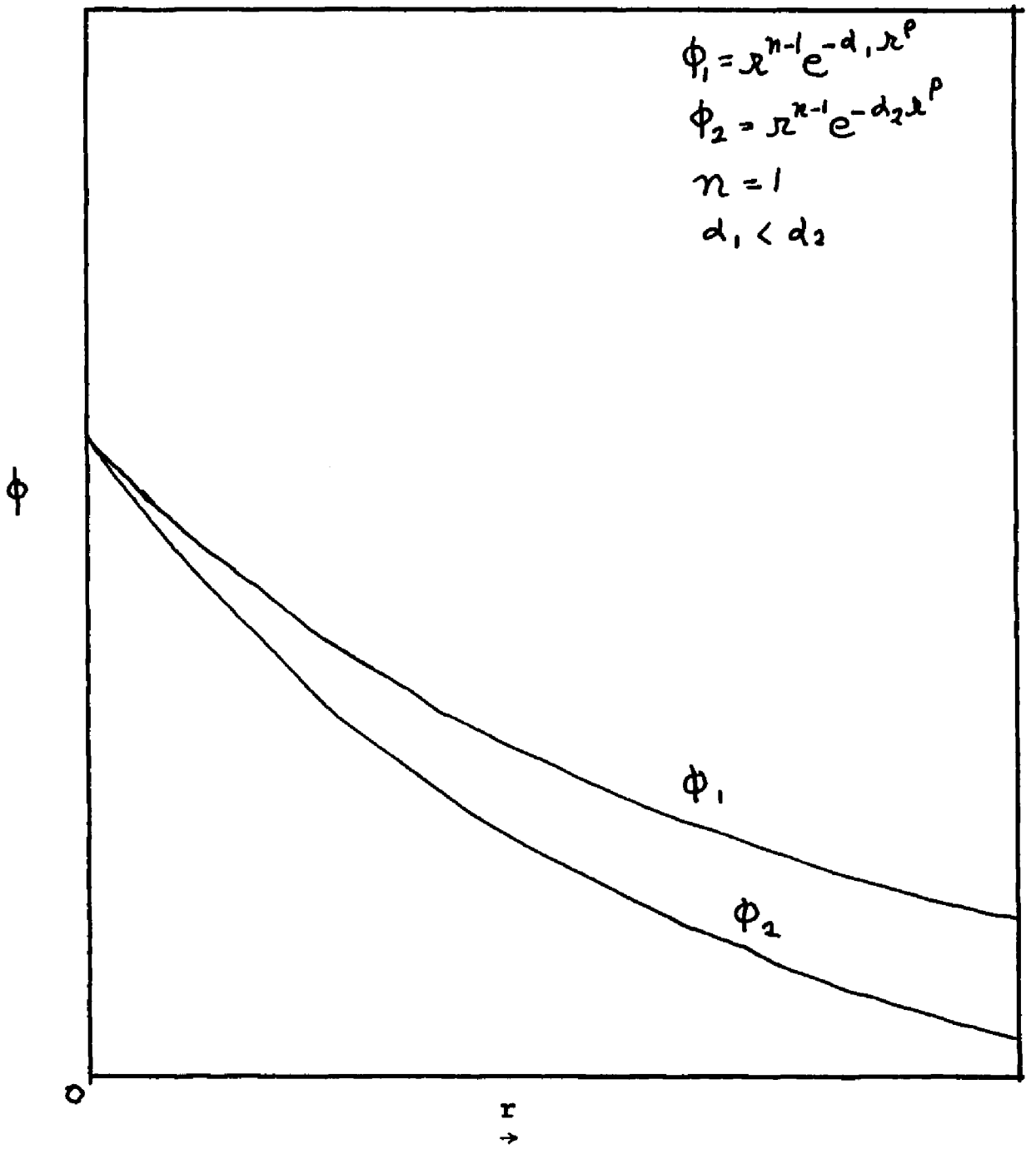


FIGURE III

THE α PARAMETER



APPENDIX II

INTEGRALS OVER GENERAL EXPONENTIAL TYPE FUNCTIONS

The details of these integrations are to be found elsewhere.[1] A quantity called the normalization constant is defined as:

$$N_i = \left(\frac{\rho (2\alpha_i)^{\frac{2n_i+1}{\rho}}}{\Gamma\left(\frac{2n_i+1}{\rho}\right)} \right)^{\frac{1}{2}} \tag{1}$$

The overlap integral is:

$$\langle \phi_i | \phi_j \rangle = N_i N_j \delta_{l_i,l_j} \delta_{m_i,m_j} \frac{\Gamma\left(\frac{n_i+n_j+1}{\rho}\right)}{\rho (\alpha_i+\alpha_j)^{\frac{n_i+n_j+1}{\rho}}} \tag{2}$$

The one electron integral is defined as:

$$\begin{aligned}(\phi_i | \phi_j) = -\tfrac{1}{2} N_i N_j \delta_{l_i,l_j} \delta_{m_i,m_j} \Bigg\{ & \frac{\Gamma\left(\frac{n_i+n_j-1}{\rho}\right)}{(\alpha_i+\alpha_j)^{\frac{n_i+n_j-1}{\rho}+2}} \cdot \\ & \Big([\alpha_i n_j - \alpha_j n_i]^2 - (\alpha_i^2 n_j + \alpha_j^2 n_i) - \\ & \alpha_i \alpha_j (\rho-1)(n_i+n_j-1) - l_i(l_i+1) \cdot \\ & (\alpha_i+\alpha_j)^2 \Big) + 2Z \frac{\Gamma\left(\frac{n_i+n_j}{\rho}\right)}{(\alpha_i+\alpha_j)^{\frac{n_i+n_j}{\rho}}} \Bigg\}\end{aligned} \tag{3}$$

Finally the electron repulsion integral is calculated to be:

$$\begin{aligned}(\phi_i \phi_j | \phi_k \phi_l) = {} & N_i N_j N_k N_l \, \delta_{\mu_{ij},\mu_{kl}} \, \delta_{M_{ik},M_{jl}} \cdot \\ & \sum_{n=\mathrm{Max}(|l_i-l_j|,|l_k-l_l|)}^{\mathrm{min}(l_i+l_j,l_k+l_l)} C^n(l_i m_i, l_j m_j) \, C^n(l_k m_k, l_l m_l) \cdot \\ & \left\{ \frac{\Gamma(s)\Gamma(t) I_{1-a}(t,s)}{\rho^2 (\alpha_i+\alpha_j)^s (\alpha_k+\alpha_l)^t} + \frac{\Gamma(u)\Gamma(v) I_a(u,v)}{\rho^2 (\alpha_i+\alpha_j)^u (\alpha_k+\alpha_l)^v} \right\}\end{aligned}$$

where $u_{ij} = l_i + l_j - 2\left[\frac{l_i + l_j}{2}\right]$

$u_{kl} = l_k + l_l - 2\left[\frac{l_k + l_l}{2}\right]$

$M_{ik} = m_i + m_k \; ; \; M_{jl} = m_j + m_l$

or $M_{ik} = m_i - m_k \; ; \; M_{jl} = m_j - m_l$ (4)

in other words if

$$m_i + m_k = m_j + m_l$$

or $$m_i - m_k = m_j - m_l$$

the Kronecker delta is set equal to one

also

$$S = (n_i + n_j - n)/p$$

$$u = (n_k + n_l - n)/p$$

$$v = (n_i + n_j + n + 1)/p$$

$$t = (n_k + n_l + n + 1)/p$$

$$a = \frac{d_i + d_j}{d_i + d_j + d_k + d_l}$$

APPENDIX III

THE ENERGY EXPRESSION FOR THE DOUBLE-ZETA WAVEFUNCTION AND ITS DERIVATIVES WITH RESPECT TO THE VARIATIONAL PARAMETERS

The double-zeta wavefunction is of the form;

$$\psi \,|\chi\bar{\chi}|$$

where
$$\chi = \phi_1 + \lambda\phi_2 \tag{1}$$

The energy expression will be written as

$$E = \frac{HN + G}{N^2}$$

where

$$H = 2(\varepsilon_{11} + 2\lambda\varepsilon_{12} + \lambda^2\varepsilon_{22})$$

$$G = J_{11} + 4\lambda G_{12} + 2\lambda^2(2K_{12} + J_{12}) + 4\lambda^3 G_{21} + \lambda^4 J_{22}$$

and
$$N = 1 + 2\lambda S + \lambda^2 . \tag{2}$$

The derivatives with respect to any non-linear parameter γ (α_i, n_i, or p) may be expressed as

$$E' = \frac{H'}{N} + \frac{HN'}{N^2} + \frac{G'}{N^2} - \frac{2GN'}{N^3}$$

where
$$H' = 2(\varepsilon_{11}' + 2\lambda\varepsilon_{12}' + \lambda^2\varepsilon_{22}')$$

$$G' = J_{11}' + 4\lambda G_{12}' + 2\lambda^2(2K_{12}' + J_{12}') + 4\lambda^3 G_{21}' + \lambda^4 J_{22}'$$

and
$$N' = 2\lambda S' \tag{3}$$

for the parameter λ

$$\frac{\partial E}{\partial \lambda} = \frac{4}{N^3}\sum_{k=1}^{5} C_k \lambda^{k-1}$$

where

$$
\begin{aligned}
C_1 &= \varepsilon_{12} - S\varepsilon_{11} + G_{12} - S J_{11} \\
C_2 &= 2S\varepsilon_{12} + \varepsilon_{22} - (1+2S^2)\varepsilon_{11} - \\
&\quad 2S G_{12} + 2K_{12} + J_{12} - J_{11} \\
C_3 &= 3S(\varepsilon_{22} - \varepsilon_{11}) + 3(G_{21} - G_{12}) \\
C_4 &= (1+2S^2)\varepsilon_{22} - 2S\varepsilon_{12} - \varepsilon_{22} + \\
&\quad 2S G_{21} - 2K_{12} - J_{12} + J_{22} \\
C_5 &= S\varepsilon_{22} - \varepsilon_{12} - G_{21} + S J_{22}
\end{aligned}
\tag{4}
$$

In the various expressions the integrals in their usual forms are

$$
\begin{aligned}
\varepsilon_{ij} &= (\phi_i | \phi_j) \\
J_{ij} &= (\phi_i \phi_i | \phi_j \phi_j) \\
K_{ij} &= (\phi_i \phi_j | \phi_j \phi_i) \\
G_{ij} &= (\phi_i \phi_i | \phi_i \phi_j)
\end{aligned}
$$

and

$$
S = \langle \phi_1 | \phi_2 \rangle \tag{5}
$$

Before proceding with the specific forms of the integrals and their derivatives we must obtain expressions for the differentials of Γ (a) and I_x(a,b). It is understood that x = x(α), a = a(n,p) and b = b(n,p).

$$
\frac{\partial \Gamma(a)}{\partial \gamma} = \Gamma(a)\,\Psi(a)\,\frac{\partial a}{\partial \gamma}
$$

where $\psi(a) = \frac{\partial [\ln \Gamma(a)]}{\partial a} = \int_0^\infty [e^{-t} - \frac{a}{1+t}] \frac{dt}{t}$; $a>0$ [73]

in fact $\frac{\partial \prod_k (\Gamma(a_k))^{n_k}}{\partial \gamma} = \prod_k (\Gamma(a_k))^{n_k} \sum_j n_j \psi(a_j) \frac{\partial a_j}{\partial \gamma}$ (6)

The differentiation with respect to the parameters α_i in the incomplete beta ratio are quite easily done with Leibnitz's rule.

$$I_x(a,b) = \frac{\Gamma(a+b)}{\Gamma(a)\Gamma(b)} \int_0^x t^{a-1}(1-t)^{b-1} dt \quad [73]$$

$$\frac{\partial I_x(a,b)}{\partial a_i} = \frac{\Gamma(a+b)}{\Gamma(a)\Gamma(b)} x^{a-1}(1-x)^{b-1} \frac{\partial x}{\partial a_i} \quad (7)$$

The differentiation with respect to γ ; n_i or p is:

$$\frac{\partial I_x(a,b)}{\partial \gamma} = \frac{\partial I_x(a,b)}{\partial a} \frac{\partial a}{\partial \gamma} + \frac{\partial I_x(a,b)}{\partial b} \frac{\partial b}{\partial \gamma} \quad (8)$$

or, introducing a notation to be used throughout,

$$\frac{\partial I_x(a,b)}{\partial \gamma} = \bar{I}_x^1(a,b) \frac{\partial a}{\partial \gamma} + \bar{I}_x^2(a,b) \frac{\partial b}{\partial \gamma}$$

1 and 2 refer to the differentiation with respect to a and b in that order. Employing the hypergeometric expansion of $I_x(a,b)$ [73]; that is

$$I_x(a,b) = \frac{\Gamma(a+b)}{\Gamma(a)\Gamma(b)} x^a \sum_{n=0}^{\infty} \frac{(1-b)_n x^n}{n!(a+n)}$$

$$\bar{I}^1_x(a,b) = I_x(a,b)(\ln x + \psi(a+b) - \psi(a)) - \frac{\Gamma(a+b)}{\Gamma(a)\Gamma(b)} x^a \sum_{n=0}^{\infty} \frac{x^n}{n!} \frac{(1-b)_n}{(a+n)^2}$$

$$\bar{I}^2_x(a,b) = I_x(a,b)(\psi(a+b) - \psi(b)) - \frac{\Gamma(a+b)}{\Gamma(a)\Gamma(b)} \cdot$$

here $$S_n(b) = (1-b)_n \sum_{m=1}^{n} \frac{1}{m-b} \qquad x^a \sum_{n=1}^{\infty} \frac{x^n}{n!} \frac{S_n(b)}{(a+n)}$$

with the recursion

$$S_{n+1}(b) = (n+1-b) S_n(b) + (1-b)_n$$

and

$$S_1(b) = 1$$

also $$(1-b)_0 = 1$$

$$(1-b)_n = \prod_{k=1}^{n} (k-b) \qquad (9)$$

In programming, the relationship $\bar{I}^k_x(a,b) = -\bar{I}^k_{1-x}(b,a)$ is used, for faster convergence the expression containing the smaller of x, and 1-x is employed. The following expressions concern themselves with ε_{ii} and J_{ii} which involve only one of the functions, therefore derivatives of these with respect to the α and n parameters of the other function are zero.

$$\varepsilon_{ii} = ((2a_i)^{\frac{2}{\rho}} (2n_i\rho - \rho + 1) \frac{1}{8} \Gamma\left(\frac{2n_i - 1}{\rho}\right) - Z(2a_i)^{\frac{1}{\rho}} \Gamma\left(\frac{2n_i}{\rho}\right) / \Gamma\left(\frac{2n_i+1}{\rho}\right))$$

$$\frac{\partial \varepsilon_{ii}}{\partial a_i} = \frac{1}{\rho a_i} \left(2\varepsilon_{ii} + Z(2a_i)^{\frac{1}{\rho}} \Gamma\left(\frac{2n_i}{\rho}\right) / \Gamma\left(\frac{2n_i+1}{\rho}\right)\right)$$

$$\frac{\partial \varepsilon_{ii}}{\partial n_i} = \frac{2}{\rho}\Big(\varepsilon_{ii}\big[\psi\big(\tfrac{2n_i-1}{\rho}\big)-\psi\big(\tfrac{n_i+1}{\rho}\big)\big] - \big[Z(2\alpha_i)^{\frac{1}{\rho}}\cdot \Gamma\big(\tfrac{2n_i}{\rho}\big)\Big(\psi\big(\tfrac{2n_i}{\rho}\big)-\psi\big(\tfrac{2n_i-1}{\rho}\big)\Big) - \frac{\rho^2}{8}(2\alpha_i)^{\frac{2}{\rho}}\cdot \Gamma\big(\tfrac{2n_i-1}{\rho}\big)\big] \Big/ \Gamma\big(\tfrac{2n_i+1}{\rho}\big)\Big)$$

$$\frac{\partial \varepsilon_{ii}}{\partial \rho} = -\frac{1}{\rho}\Big(\big[\psi\big(\tfrac{2n_i-1}{\rho}\big)\big(\tfrac{2n_i-1}{\rho}\big)-\psi\big(\tfrac{2n_i+1}{\rho}\big)\big(\tfrac{2n_i+1}{\rho}\big)+\frac{2}{\rho}\cdot \ln(2\alpha_i)\big]\varepsilon_{ii} - Z(2\alpha_i)^{\frac{1}{\rho}}\Gamma\big(\tfrac{2n_i}{\rho}\big)\Big/\Gamma\big(\tfrac{2n_i+1}{\rho}\big)\cdot \Big[\psi\big(\tfrac{2n_i}{\rho}\big)\big(\tfrac{2n_i}{\rho}\big)-\psi\big(\tfrac{2n_i-1}{\rho}\big)\big(\tfrac{2n_i-1}{\rho}\big)-\frac{1}{\rho}\ln(2\alpha_i)\Big] + \big(\tfrac{2n_i-1}{8}\big)(2\alpha_i)^{\frac{2}{\rho}}\Gamma\big(\tfrac{2n_i}{\rho}\big)\Big/\Gamma\big(\tfrac{2n_i+1}{\rho}\big)\Big)$$

$$J_{ii} = 2(2\alpha_i)^{\frac{1}{\rho}}\Gamma\big(\tfrac{2n_i}{\rho}\big)\Big/\Gamma\big(\tfrac{2n_i+1}{\rho}\big)\, I_{\frac{1}{2}}\big(\tfrac{2n_i+1}{\rho}, \tfrac{2n_i}{\rho}\big)$$

$$\frac{\partial J_{ii}}{\partial \alpha_i} = \frac{1}{\alpha_i \rho} J_{ii}$$

$$\frac{\partial J_{ii}}{\partial n_i} = \frac{2}{\rho}\Big(\big[\psi\big(\tfrac{2n_i}{\rho}\big)-\psi\big(\tfrac{2n_i+1}{\rho}\big)\big]J_{ii} + 2(2\alpha_i)^{\frac{1}{\rho}}\cdot \Gamma\big(\tfrac{2n_i}{\rho}\big)\Big/\Gamma\big(\tfrac{2n_i+1}{\rho}\big)\Big(\bar{I}^{1}_{\frac{1}{2}}\big(\tfrac{2n_i+1}{\rho}, \tfrac{2n_i}{\rho}\big)+\bar{I}^{2}_{\frac{1}{2}}\big(\tfrac{2n_i+1}{\rho}, \tfrac{2n_i}{\rho}\big)\Big)\Big)$$

$$\frac{\partial J_{ii}}{\partial \rho} = -\frac{J_{ii}}{\rho}\Big[\frac{1}{\rho}\ln(2\alpha_i)+\psi\big(\tfrac{2n_i}{\rho}\big)\big(\tfrac{2n_i}{\rho}\big)-\psi\big(\tfrac{2n_i+1}{\rho}\big)\big(\tfrac{2n_i+1}{\rho}\big) + \Big(\big(\tfrac{2n_i+1}{\rho}\big)\bar{I}^{1}_{\frac{1}{2}}\big(\tfrac{2n_i+1}{\rho}, \tfrac{2n_i}{\rho}\big)+\big(\tfrac{2n_i}{\rho}\big)\bar{I}^{2}_{\frac{1}{2}}\big(\tfrac{2n_i+1}{\rho}, \tfrac{2n_i}{\rho}\big)\Big)\Big/ I_{\frac{1}{2}}\big(\tfrac{2n_i+1}{\rho}, \tfrac{2n_i}{\rho}\big)\Big] \qquad (10)$$

The expressions revolving around S, ε_{ij}, J_{ij}, K_{ij} are symmetrical in both ϕ_i and ϕ_j.

$$C = \big((2\alpha_1)^{\frac{2n_1+1}{\rho}}(2\alpha_2)^{\frac{2n_2+1}{\rho}}\big)^{\frac{1}{2}}\Big/(\alpha_1+\alpha_2)^{\frac{n_1+n_2+1}{\rho}}$$

$$C' = \frac{C}{\Big(\Gamma\big(\tfrac{2n_1+1}{\rho}\big)\Gamma\big(\tfrac{2n_2+1}{\rho}\big)\Big)^{\frac{1}{2}}}$$

$$S = C'\,\Gamma\big(\tfrac{n_1+n_2+1}{\rho}\big)$$

$$\frac{\partial S}{\partial d_i} = \frac{S}{\rho}\left(\frac{2n_i+1}{2d_i} - \frac{n_1+n_2+1}{d_1+d_2}\right)$$

$$\frac{\partial S}{\partial n_i} = \frac{S}{\rho}\left(\psi\left(\frac{n_1+n_2+1}{\rho}\right) - \psi\left(\frac{2n_i+1}{\rho}\right) + \ln\left(\frac{2d_i}{d_1+d_2}\right)\right)$$

$$\frac{\partial S}{\partial \rho} = -\frac{S}{\rho}\left(\ln C - \tfrac{1}{2}\psi\left(\tfrac{2n_1+1}{\rho}\right)\left(\tfrac{2n_1+1}{\rho}\right) - \tfrac{1}{2}\psi\left(\tfrac{2n_2+1}{\rho}\right)\left(\tfrac{2n_2+1}{\rho}\right) + \psi\left(\tfrac{n_1+n_2+1}{\rho}\right)\left(\tfrac{n_1+n_2+1}{\rho}\right)\right)$$

$$\varepsilon_{ij} = C'\left(-\tfrac{1}{2}\left([d_i n_j - d_j n_i]^2 - [d_i^2 n_j + d_j^2 n_i] - d_i d_j(\rho-1)(n_i+n_j-1)\right)\Gamma\left(\tfrac{n_i+n_j-1}{\rho}\right)(d_i+d_j)^{\frac{2}{\rho}-2} - Z\,(d_i+d_j)^{\frac{1}{\rho}}\Gamma\left(\tfrac{n_i+n_j}{\rho}\right)\right)$$

$$\frac{\partial \varepsilon_{ij}}{\partial d_i} = \left(\frac{2d_i+1}{2d_i\rho} - \frac{d_i+d_j-1}{\rho(d_i+d_j)} - \frac{2}{d_i+d_j}\right)\varepsilon_{ij} + (d_i+d_j)^{\frac{1}{\rho}-2}\cdot C'\left((d_i+d_j)^{\frac{1}{\rho}}\Gamma\left(\tfrac{n_i+n_j-1}{\rho}\right)\left[\tfrac{d_j}{2}(2n_i n_j + (\rho-1)\cdot(n_i+n_j-1)) - d_i n_j(n_j-1)\right] + Z\,(d_i+d_j)\cdot\left(\tfrac{1}{\rho}-2\right)\Gamma\left(\tfrac{n_i+n_j}{\rho}\right)\right)$$

$$\frac{\partial \varepsilon_{ij}}{\partial n_i} = \frac{1}{\rho}\varepsilon_{ij}\left[\psi\left(\tfrac{n_i+n_j-1}{\rho}\right) - \psi\left(\tfrac{2n_i+1}{\rho}\right) + \ln\left(\tfrac{2d_i}{d_i+d_j}\right)\right] + C'\left[(d_i+d_j)^{\frac{2}{\rho}-2}\Gamma\left(\tfrac{n_i+n_j-1}{\rho}\right)\left(d_i d_j\left(n_j + \tfrac{1}{2}(\rho-1)\right) + d_j^2\left(\tfrac{1}{2}-n_i\right)\right) - \frac{Z}{\rho}(d_i+d_j)^{\frac{1}{\rho}}\Gamma\left(\tfrac{n_i+n_j}{\rho}\right)\cdot\left(\psi\left(\tfrac{n_i+n_j}{\rho}\right) - \psi\left(\tfrac{n_i+n_j-1}{\rho}\right)\right)\right]$$

$$\frac{\partial \varepsilon_{ij}}{\partial p} = -\frac{1}{p}\Big([\ln c - \tfrac{1}{2}\psi(\tfrac{2n_i+1}{p})(\tfrac{2n_i+1}{p}) + \tfrac{2}{p}\ln(d_i+d_j) - \tfrac{1}{2}\psi(\tfrac{2n_j+1}{p})(\tfrac{2n_j+1}{p}) + \psi(\tfrac{n_i+n_j+1}{p})(\tfrac{n_i+n_j+1}{p})]\varepsilon_{ij} - 2c'(d_i+d_j)^{\frac{1}{p}}\Gamma(\tfrac{n_i+n_j}{p})[\psi(\tfrac{n_i+n_j}{p})(\tfrac{n_i+n_j}{p}) - \psi(\tfrac{n_i+n_j-1}{p})(\tfrac{n_i+n_j-1}{p}) - \tfrac{1}{2}\ln(d_i+d_j)]) + \tfrac{1}{2}c'd_id_j(d_i+d_j)^{\frac{2}{p}-2}(n_i+n_j-1)\Gamma(\tfrac{n_i+n_j-1}{p})$$

$$J_{ij} = (2d_i)^{\frac{1}{p}}\Gamma(\tfrac{2n_i}{p})/\Gamma(\tfrac{2n_i+1}{p})\, I_{\frac{d_j}{d_i+d_j}}(\tfrac{2n_j+1}{p}, \tfrac{2n_i}{p}) + (2d_j)^{\frac{1}{p}}\Gamma(\tfrac{2n_j}{p})/\Gamma(\tfrac{2n_j+1}{p})\, I_{\frac{d_i}{d_i+d_j}}(\tfrac{2n_i+1}{p}, \tfrac{2n_j}{p})$$

$$\frac{\partial J_{ij}}{\partial d_i} = \frac{1}{pd_i}(2d_i)^{\frac{1}{p}}\Gamma(\tfrac{2n_i}{p})/\Gamma(\tfrac{2n_i+1}{p})\, I_{\frac{d_j}{d_i+d_j}}(\tfrac{2n_j+1}{p}, \tfrac{2n_i}{p})$$

$$\frac{\partial J_{ij}}{\partial n_i} = \frac{2}{p}\Big((2d_i)^{\frac{1}{p}}\Gamma(\tfrac{2n_i}{p})/\Gamma(\tfrac{2n_i+1}{p})\Big[I_{\frac{d_j}{d_i+d_j}}(\tfrac{2n_j+1}{p}, \tfrac{2n_i}{p})\cdot(\psi(\tfrac{2n_i}{p}) - \psi(\tfrac{2n_i+1}{p})) + \bar{I}^{2}_{\frac{d_j}{d_i+d_j}}(\tfrac{2n_j+1}{p}, \tfrac{2n_i}{p})\Big] + (2d_j)^{\frac{1}{p}}\Gamma(\tfrac{2n_j}{p})/\Gamma(\tfrac{2n_j+1}{p})\,\bar{I}^{1}_{\frac{d_i}{d_i+d_j}}(\tfrac{2n_i+1}{p}, \tfrac{2n_j}{p})\Big)$$

$$\frac{\partial J_{ij}}{\partial p} = -\frac{1}{p}(2d_i)^{\frac{1}{p}}\Gamma(\tfrac{2n_i}{p})/\Gamma(\tfrac{2n_i+1}{p})\,\dot{I}_{\frac{d_j}{d_i+d_j}}(\tfrac{2n_j+1}{p}, \tfrac{2n_i}{p})\cdot\Big(\tfrac{1}{p}\ln(2d_i) + \psi(\tfrac{2n_i}{p})(\tfrac{2n_i}{p}) - \psi(\tfrac{2n_i+1}{p})(\tfrac{2n_i+1}{p}) + (\bar{I}^{1}_{\frac{d_j}{d_i+d_j}}(\tfrac{2n_j+1}{p}, \tfrac{2n_i}{p})(\tfrac{2n_j+1}{p}) + \bar{I}^{2}_{\frac{d_j}{d_i+d_j}}(\tfrac{2n_j+1}{p}, \tfrac{2n_i}{p})(\tfrac{2n_i}{p}))/ I_{\frac{d_j}{d_i+d_j}}(\tfrac{2n_j+1}{p}, \tfrac{2n_i}{p}) - \tfrac{1}{p}(2d_j)^{\frac{1}{p}}\Gamma(\tfrac{2n_j}{p})/\Gamma(\tfrac{2n_j+1}{p})\cdot I_{\frac{d_i}{d_i+d_j}}(\tfrac{2n_i+1}{p}, \tfrac{2n_j}{p})\Big(\tfrac{1}{p}\ln(2d_j) + \psi(\tfrac{2n_j}{p})(\tfrac{2n_j}{p}) -$$

$$\psi\left(\frac{2n_j+1}{\rho}\right)\left(\frac{2n_j+1}{\rho}\right)+\left(\bar{I}^{1}_{\frac{d_i}{d_i+d_j}}\left(\frac{2n_i+1}{\rho},\frac{2n_j}{\rho}\right)\left(\frac{2n_i+1}{\rho}\right)+\bar{I}^{2}_{\frac{d_i}{d_i+d_j}}\left(\frac{2n_i+1}{\rho},\frac{2n_j}{\rho}\right)\left(\frac{2n_j}{\rho}\right)\right)/I_{\frac{d_i}{d_i+d_j}}\left(\frac{2n_i+1}{\rho},\frac{2n_j}{\rho}\right)$$

$$K_{ij} = 2C'^{2}(d_i+d_j)^{\frac{1}{\rho}}\Gamma\left(\frac{n_i+n_j}{\rho}\right)\Gamma\left(\frac{n_i+n_j+1}{\rho}\right)I_{\frac{1}{2}}\left(\frac{n_i+n_j+1}{\rho},\frac{n_i+n_j}{\rho}\right)$$

$$\frac{\partial K_{ij}}{\partial d_i} = \frac{2}{\rho}\left(\frac{2n_i+1}{2d_i}-\frac{n_i+n_j}{d_i+d_j}+\frac{1}{2(d_i+d_j)}\right)K_{ij}$$

$$\frac{\partial K_{ij}}{\partial n_i} = \frac{1}{\rho}\Big(K_{ij}\left(\psi\left(\frac{n_i+n_j}{\rho}\right)+\psi\left(\frac{n_i+n_j+1}{\rho}\right)-2\psi\left(\frac{2n_i+1}{\rho}\right)+2\ln\left(\frac{2d_i}{d_i+d_j}\right)\right)+2C'^{2}(d_i+d_j)^{\frac{1}{\rho}}\Gamma\left(\frac{n_i+n_j+1}{\rho}\right)\cdot\Gamma\left(\frac{n_i+n_j}{\rho}\right)\left(\bar{I}^{1}_{\frac{1}{2}}\left(\frac{n_i+n_j+1}{\rho},\frac{n_i+n_j}{\rho}\right)+\bar{I}^{2}_{\frac{1}{2}}\left(\frac{n_i+n_j+1}{\rho},\frac{n_i+n_j}{\rho}\right)\right)$$

$$\frac{\partial K_{ij}}{\partial \rho} = \frac{1}{\rho}K_{ij}\Big(2\ln C-\psi\left(\frac{2n_i+1}{\rho}\right)\left(\frac{2n_i+1}{\rho}\right)-\psi\left(\frac{2n_j+1}{\rho}\right)\left(\frac{2n_j+1}{\rho}\right)+\frac{1}{\rho}\ln(d_i+d_j)+\psi\left(\frac{n_i+n_j}{\rho}\right)\left(\frac{n_i+n_j}{\rho}\right)+\psi\left(\frac{n_i+n_j+1}{\rho}\right)\left(\frac{n_i+n_j+1}{\rho}\right)+\left(\bar{I}^{1}_{\frac{1}{2}}\left(\frac{n_i+n_j+1}{\rho},\frac{n_i+n_j}{\rho}\right)\cdot\left(\frac{n_i+n_j+1}{\rho}\right)+\bar{I}^{2}_{\frac{1}{2}}\left(\frac{n_i+n_j+1}{\rho},\frac{n_i+n_j}{\rho}\right)\left(\frac{n_i+n_j}{\rho}\right)\right)/I_{\frac{1}{2}}\left(\frac{n_i+n_j+1}{\rho},\frac{n_i+n_j}{\rho}\right)\Big).$$

(11)

The following forms derived from G_{ij} are not symmetrical in ϕ_i and ϕ_j.

$$G_{ij} = C'\left(\Gamma\left(\frac{n_i+n_j+1}{\rho}\right)\Gamma\left(\frac{2n_i}{\rho}\right)/\Gamma\left(\frac{2n_i+1}{\rho}\right)(2\alpha_i)^{\frac{1}{\rho}}\cdot I_{\frac{\alpha_i+\alpha_j}{3\alpha_i+\alpha_j}}\left(\frac{n_i+n_j+1}{\rho},\frac{2n_i}{\rho}\right)+(\alpha_i+\alpha_j)^{\frac{1}{\rho}} I_{\frac{2\alpha_i}{3\alpha_i+\alpha_j}}\left(\frac{2n_i+1}{\rho},\frac{n_i+n_j}{\rho}\right)\right)$$

$$\frac{\partial G_{ij}}{\partial \alpha_i} = \frac{1}{\rho}G_{ij}\left(\frac{2n_i+1}{2\alpha_i}-\frac{n_i+n_j}{\alpha_i+\alpha_j}\right)+C'\left(\frac{\alpha_j(2\alpha_i)^{\frac{1}{\rho}}}{\rho\alpha_i(\alpha_i+\alpha_j)}\right)\cdot \Gamma\left(\frac{2n_i}{\rho}\right)/\Gamma\left(\frac{2n_i+1}{\rho}\right) I_{\frac{\alpha_i+\alpha_j}{3\alpha_i+\alpha_j}}\left(\frac{n_i+n_j+1}{\rho},\frac{2n_i}{\rho}\right)$$

$$\frac{\partial G_{ij}}{\partial \alpha_j} = \frac{1}{\rho}G_{ij}\left(\frac{2n_i+1}{2\alpha_i}-\frac{n_i+n_j}{\alpha_i+\alpha_j}\right)-C'\frac{(2\alpha_i)^{\frac{1}{\rho}}}{\rho(\alpha_i+\alpha_j)}\cdot \Gamma\left(\frac{2n_i}{\rho}\right)/\Gamma\left(\frac{2n_i+1}{\rho}\right) I_{\frac{\alpha_i+\alpha_j}{3\alpha_i+\alpha_j}}\left(\frac{n_i+n_j+1}{\rho},\frac{2n_i}{\rho}\right)$$

$$\frac{\partial G_{ij}}{\partial n_i} = \frac{1}{\rho}\left(\left(\ln\frac{2\alpha_i}{\alpha_i+\alpha_j}-\psi\left(\frac{2n_i+1}{\rho}\right)+\psi\left(\frac{n_i+n_j}{\rho}\right)\right)G_{ij}+\left(2\psi\left(\frac{2n_i}{\rho}\right)-2\psi\left(\frac{2n_i+1}{\rho}\right)+\psi\left(\frac{n_i+n_j+1}{\rho}\right)-\psi\left(\frac{n_i+n_j}{\rho}\right)\right)\frac{C'}{\rho^2}(2\alpha_i)^{\frac{1}{\rho}}\Gamma\left(\frac{2n_i}{\rho}\right)/\Gamma\left(\frac{2n_i+1}{\rho}\right)\cdot I_{\frac{\alpha_i+\alpha_j}{3\alpha_i+\alpha_j}}\left(\frac{n_i+n_j+1}{\rho},\frac{2n_i}{\rho}\right)+C'(2\alpha_i)^{\frac{1}{\rho}}\cdot \Gamma\left(\frac{2n_i}{\rho}\right)/\Gamma\left(\frac{2n_i+1}{\rho}\right)\cdot\Gamma\left(\frac{n_i+n_j+1}{\rho}\right)\cdot\left(\bar{I}^{1}_{\frac{\alpha_i+\alpha_j}{3\alpha_i+\alpha_j}}\left(\frac{n_i+n_j+1}{\rho},\frac{2n_i}{\rho}\right)+2\bar{I}^{2}_{\frac{\alpha_i+\alpha_j}{3\alpha_i+\alpha_j}}\left(\frac{n_i+n_j+1}{\rho},\frac{2n_i}{\rho}\right)\right)+C'(\alpha_i+\alpha_j)^{\frac{1}{\rho}}\Gamma\left(\frac{n_i+n_j}{\rho}\right)\left(2\bar{I}^{1}_{\frac{2\alpha_i}{3\alpha_i+\alpha_j}}\left(\frac{2n_i+1}{\rho},\frac{n_i+n_j}{\rho}\right)+\bar{I}^{2}_{\frac{2\alpha_i}{3\alpha_i+\alpha_j}}\left(\frac{2n_i+1}{\rho},\frac{n_i+n_j}{\rho}\right)\right)$$

$$\frac{\partial G_{ij}}{\partial n_j} = \frac{1}{\rho}\Big(\Big(\ln\frac{2d_j}{d_i+d_j} - \psi\Big(\frac{2n_j+1}{\rho}\Big) + \psi\Big(\frac{2n_j}{\rho}\Big)\Big) G_{ij} +$$
$$\Big(\psi\Big(\frac{n_i+n_j+1}{\rho}\Big) - \psi\Big(\frac{n_i+n_j}{\rho}\Big)\Big)\frac{c'}{\rho^2}(2d_i)^{\frac{1}{\rho}}\Gamma\Big(\frac{2n_j}{\rho}\Big)/\Gamma\Big(\frac{2n_j+1}{\rho}\Big)\cdot$$
$$I_{\frac{d_i+d_j}{3d_i+d_j}}\Big(\frac{n_i+n_j+1}{\rho}, \frac{2n_i}{\rho}\Big) + c'(2d_i)^{\frac{1}{\rho}}\Gamma\Big(\frac{n_i+n_j+1}{\rho}\Big)\cdot$$
$$\Gamma\Big(\frac{2n_i}{\rho}\Big)/\Gamma\Big(\frac{2n_i+1}{\rho}\Big)\bar{I}^{1}_{\frac{d_i+d_j}{3d_i+d_j}}\Big(\frac{n_i+n_j+1}{\rho}, \frac{2n_i}{\rho}\Big) +$$
$$c'(d_i+d_j)^{\frac{1}{\rho}}\Gamma\Big(\frac{n_i+n_j}{\rho}\Big)\bar{I}^{2}_{\frac{2d_i}{3d_i+d_j}}\Big(\frac{2n_i+1}{\rho}, \frac{n_i+n_j}{\rho}\Big)\Big)$$

$$\frac{\partial G_{ij}}{\partial \rho} = \frac{1}{\rho}\Big(\Big(\ln C - \frac{1}{2}\psi\Big(\frac{2n_i+1}{\rho}\Big)\Big(\frac{2n_i+1}{\rho}\Big) - \frac{1}{2}\psi\Big(\frac{2n_j+1}{\rho}\Big)\Big(\frac{2n_j+1}{\rho}\Big)\Big) G_{ij} +$$
$$c'\Big\{(2d_i)^{\frac{1}{\rho}}\Gamma\Big(\frac{n_i+n_j+1}{\rho}\Big)\Gamma\Big(\frac{2n_i}{\rho}\Big)/\Gamma\Big(\frac{2n_i+1}{\rho}\Big)\cdot$$
$$I_{\frac{d_i+d_j}{3d_i+d_j}}\Big(\frac{n_i+n_j+1}{\rho}, \frac{2n_i}{\rho}\Big)\Big[\psi\Big(\frac{2n_i}{\rho}\Big)\Big(\frac{2n_i}{\rho}\Big) - \psi\Big(\frac{2n_i+1}{\rho}\Big)\Big(\frac{2n_i+1}{\rho}\Big) +$$
$$\psi\Big(\frac{n_i+n_j+1}{\rho}\Big)\Big(\frac{n_i+n_j+1}{\rho}\Big) + \frac{1}{\rho}\ln(2d_i) +$$
$$\Big(\bar{I}^{1}_{\frac{d_i+d_j}{3d_i+d_j}}\Big(\frac{n_i+n_j+1}{\rho}, \frac{2n_i}{\rho}\Big)\Big(\frac{n_i+n_j+1}{\rho}\Big) + \bar{I}^{2}_{\frac{d_i+d_j}{3d_i+d_j}}\Big(\frac{n_i+n_j+1}{\rho}, \frac{2n_i}{\rho}\Big)\cdot$$
$$\Big(\frac{2n_i}{\rho}\Big)\Big)/I_{\frac{d_i+d_j}{3d_i+d_j}}\Big(\frac{n_i+n_j+1}{\rho}, \frac{2n_i}{\rho}\Big)\Big] + (d_i+d_j)^{\frac{1}{\rho}}\cdot$$
$$\Gamma\Big(\frac{n_i+n_j}{\rho}\Big)I_{\frac{2d_i}{3d_i+d_j}}\Big(\frac{2n_i+1}{\rho}, \frac{n_i+n_j}{\rho}\Big)\Big[\psi\Big(\frac{n_i+n_j}{\rho}\Big)\Big(\frac{n_i+n_j}{\rho}\Big) +$$
$$\frac{1}{\rho}\ln(d_i+d_j) + \Big(\bar{I}^{1}_{\frac{2d_i}{3d_i+d_j}}\Big(\frac{2n_i+1}{\rho}, \frac{n_i+n_j}{\rho}\Big)\Big(\frac{2n_i+1}{\rho}\Big) +$$
$$\bar{I}^{2}_{\frac{2d_i}{3d_i+d_j}}\Big(\frac{2n_i+1}{\rho}, \frac{n_i+n_j}{\rho}\Big)\Big(\frac{n_i+n_j}{\rho}\Big)\Big)/I_{\frac{2d_i}{3d_i+d_j}}\Big(\frac{2n_i+1}{\rho}, \frac{n_i+n_j}{\rho}\Big)\Big]\Big\}\Big).$$

(12)